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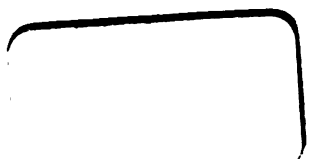

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Paper No. 164

SYMPOSIUM ON IRON AND STEEL.

Edited by

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IRON AND STEEL CASTINGS.

By

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Iron and steel castings may be made of (1) steel, (2) malleable iron, or (3) cast iron. Though there are a number of trade names for particular sorts of metal sold in the form of castings, yet all belong to one of these three classes—which have distinctive properties, are manufactured by different processes, and have different fields of usefulness. We hear, for instance, of "semi-steel", "gun-iron" or "wrought-iron" castings; however, these are but special sorts of castings—the first two of grey iron, the last of steel castings.

Steel castings are made of steel, which may be hard or soft, of high or low carbon, with or without special alloys, just as steel forgings or rolled steel shapes are made of different sorts of steel. Cast-iron castings, of course, are composed chiefly of pig iron, generally remelted, and are distinguished by the comparatively low tensile strength and almost total lack of ductility characteristic of that metal, which is attributable largely to its high content of carbon. In some sorts of iron castings, part or all of the metal is made almost glass-hard by casting it against an iron chill, whereby the carbon is retained in the "combined" state as carbide of iron, an intensely hard

substance. But in most cases iron castings are comparatively soft and readily machinable, and at least a considerable part of the carbon is in the form of flakes of graphite, which are distributed through the metal as flakes of mica might be mixed in mortar, destroying its continuity and rendering it weak and brittle.

Malleable iron might be called a mongrel iron. When first cast, the metal throughout its cross-section is very hard and is identical in nature with the chilled portion of a chilled-iron casting. By heating this hard, brittle metal for many hours at a full red heat, it is made soft and quite ductile. The combined carbon is thereby all converted to graphite, which, however, is in the form of globular aggregations of very fine powder and is not in flakes, as in grey iron. The portion of the metal near the surface of the castings, moreover, is made nearly carbonless. Thus the metal is practically dead-soft steel whose continuity is broken up by aggregations of a strengthless material. It is, therefore, quite ductile and has a fair degree of strength, but, naturally, is not as strong or as ductile as dead-soft steel.

From this brief statement of the general nature of the three metals, we see that they necessarily have distinct fields of usefulness. We use steel or malleable-iron castings when we need a metal with a considerable amount of strength and ductility: in most cases, indeed, our reason for using a casting, instead of forming the piece of rolled or forged metal, is that it can not be so made; or because the expense of the rolling, forging, or cold-shaping of steel plate would be prohibitive. Many times the choice between a steel casting and a drop forging, for instance, is dictated simply by the number of pieces we shall require; if we need a great many, we can afford to make dies, and we secure a better, and often cheaper, article; whereas, if there are but a few required, we are constrained to use castings because of the expense involved in the purchase of forging dies.

When we order cast-iron castings, on the other hand, we generally wish to use them for parts in which great strength is not required—often because the weight of the piece is of no consequence, or even because a heavy piece is an absolute essential. By using a large piece of comparatively weak and brittle metal we secure the total strength required. The metal, more-

over, is very strong against compressive stresses, and is often used to resist such stresses in cases where comparatively heavy sections can be tolerated.

The choice between steel and malleable-iron castings is dictated partly by their respective properties, partly by price, and partly by the limitations of the processes by which malleable iron is made. As already stated, steel is, in its nature, a more homogeneous metal, and therefore tougher and stronger than malleable iron. Moreover, castings of malleable iron are somewhat prone to actual porosity or sponginess at the center, especially in certain portions of irregular castings, so that for this reason, also, a steel casting is stronger and more reliable. Finally, malleable iron can be made only into castings of quite light sections; whereas, there is almost no limit to the size and weight of steel castings that can be produced. For uses where only a fair amount of strength and toughness are necessary, and the casting is, therefore, of light section, it often pays to buy malleable castings, because they are cheaper than steel.

The variations in the properties of steel castings are due (1) to variations in the composition of the steel, (2) to the annealing or heat treatment to which the steel is subjected, and (3) to the soundness of the casting. The last of these may be summarized in the familiar saying, "a casting is always a casting", by which the "initiated" mean that it may always contain hidden blow-holes or shrinkage cavities that cause or aid its failure when least expected. The gases that are liberated from solidifying steel, of course, cause blow-holes in ingots as well as in castings, but by the time the ingot is reduced to the rolled or forged shape, these holes are at least closed up, if not partially welded—and they are generally so located as to be least harmful to the finished piece. In the case of castings, the gas from the metal and the steam and gas set free from the sand mould may cause blow-holes that can not be detected by surface inspection of the piece.

Because steel and iron contract in cooling, moreover, there is a tendency toward the formation of a cavity in the upper portion of almost any mass of metal during its cooling from the liquid state to atmospheric temperature. In rolled and forged work we get rid of the hollow part of the ingot simply by not

using it. In castings, however, especially steel castings, we provide against these cavities by putting extra portions upon the piece, which are so shaped and located that they, and not the casting itself, shall be hollow. The metal drained from these "sink-heads" feeds the shrinkage of the casting, and they are knocked or cut from the piece after it has grown cold. Failure to properly locate or design these heads will almost certainly give rise to shrinkage cavities of greater or less size in the casting; and if these are so located as not to be discovered and welded up, we have a hidden source of weakness in our casting.

The most important constituent of steel, upon which the nature of the metal largely depends, is carbon. Depending upon the carbon content, ordinary steel castings vary from very soft to dead-hard steel. The carbon content in each class of steel castings is approximately as follows:

Class	C. %	Special Trade Names
Very soft	up to 0.15	Wrought-Iron Castings
Soft	0.15 to 0.30	.....
Medium	0.30 to 0.40	.....
Hard	0.40 up	40-Point Steel

The effect of silicon in steel castings is chiefly to promote soundness and to discourage the formation of blow-holes. The average silicon content of steel castings is from 0.25 to 0.40 percent, though in "very soft" steel it is sometimes as low as 0.15, or even 0.10 percent. The silicon content should not be specified by the purchaser but left to the judgment of the maker.

Manganese, in "very soft" steel castings, is sometimes as low as 0.20%, but in the average casting it runs from about 0.40% to 0.80%, or even higher. As manganese additions are absolutely essential in the manufacture of steel, and in most cases the steel could not be made sound at all without it, the manufacturer is in a position to know how much he should use and should not be hampered by limits imposed in specifications.

The effect of phosphorus in steel is to produce brittleness in the metal when cold. Hence the limits are sharply specified. No steel casting should contain over 0.10% phosphorus, and

0.08% is better. For high-grade castings the upper limit is generally 0.05%.

Sulphur is a harmful impurity in steel, its chief effect being to make the metal "red-short", or weak and brittle when hot. Steel that has to be rolled, forged or quenched from a red heat in hardening, therefore, must contain as little sulphur as possible. As the purchaser of steel castings very seldom forges them at all, or subjects them to hardening processes, many makers of steel castings contend that the sulphur content should not be specified. As they point out, the almost inevitable effect of too much sulphur in their steel is that the castings will crack when hot under the stresses set up during the cooling, so that there is no incentive for the steel maker to take chances on the use of steel of too high a sulphur content. They contend, therefore, that they should be allowed to settle the sulphur content of their steel for themselves, as they will be sure not to allow too high a content and should not be embarrassed by specifications that may call for a much lower sulphur content than is really necessary, at an added expense to them. Most specifications for steel castings, however, contain a maximum limit for sulphur, usually from 0.05% to 0.06%.

The effect of annealing and heat-treatment, in general, is more marked in high-carbon than in low-carbon steel. One effect, however, that is practically as great in soft as in hard steels, is to relieve the stresses that are set up by the unequal rates of cooling of parts of a casting of varying cross-section. As soft steel contracts more in cooling than does hard steel, the stresses are generally somewhat greater in soft castings. This is offset by the fact that as the steel is tougher it can have more stresses in it without danger of failure; so that the question of stress is nearly as important in a soft as in a hard casting. Able metallurgists have contended that soft-steel castings need no annealing, but the tendency has long been to anneal more, rather than less, often.

Plain annealing, that is, heating the casting to a given temperature, which is maintained for some time, and then cooling it slowly, breaks up the coarse micro-structure characteristic of steel in the cast condition and substitutes for it a much finer and more uniform structure. The result is to raise the strength

and elastic limit of the casting, to a degree that is generally the greater the higher the carbon content of the metal—the strength of very soft castings being raised very little by annealing. The toughness of the metal, as measured by its extension and contraction of area in the tensile test, is also increased—more in high carbon than in low carbon steel. As measured by bending tests, the toughness is also greatly increased; and though hard steels are improved more than soft, yet the difference between an annealed and an unannealed soft-steel casting is usually greater in the bending test than in extension or contraction of area.

Heat treatment, that is, heating the casting to a given temperature for a given time, to relieve cooling stresses and remove the coarse micro-structure of the cast metal; cooling more or less rapidly, to partially or entirely harden the metal; and reheating to relieve the hardening stresses and to "draw" part of the hardness, is, of late, being practiced to an increasing extent. Its effect is similar to that of plain annealing, but more marked. The strength and toughness of the steel are greatly increased, the effect upon the lower carbon steels being more marked than is that of plain annealing. This is especially true of the resistance to sudden shock. A dead-soft steel, of so low a carbon content that the effect on the strength of even a drastic heat treatment is hardly noticeable, is made several fold as resistant to shock tests as it is in the annealed condition.

The method by which the steel is made influences its properties, largely by its effect upon the composition that it is possible to secure, and upon the tendency of the steel to unsoundness. The "basic" processes, by which are meant those in which the slag can be so regulated as to permit the removal of most of the phosphorus and sulphur of the steel, naturally enable the manufacturer to secure low phosphorus and sulphur content, whereby the steel is made tougher when cold and less prone to shrinkage cracks. When the steel is made by "acid" processes, on the other hand, purity must be attained by the use of pure raw materials, at an increased cost. Moreover, lower phosphorus and sulphur content are secured by basic processes than it is possible to attain by acid processes.

Again, the extent to which the steel is subjected to oxida-

tion during its manufacture influences the tendency to unsoundness. It may be said, in general, that the Bessemer process oxidizes the steel to the greatest extent, the open-hearth process to a less degree, the crucible process to a still less degree, and the electric-furnace process least of all. The processes by which the steel may be made and their more marked characteristics are as follows:

Process	Nature	Remarks
Bessemer (generally baby vessels)	acid	Very oxidizing.
Open-hearth	basic	Generally thought to be less oxidizing than the Bessemer.
Open-hearth	acid	Less oxidizing than either of the above.
Crucible	acid	Hardly oxidizing at all.
Electric	acid basic	Not oxidizing. Oxidation of steel made by other processes may be corrected by final treatment in the electric furnace.

It is not possible to state dogmatically that one process produces better steel than another, because the raw material used and the skill of the operator vary to a considerable extent. Even with the electric furnace, very poor steel can be produced by inexperienced men; though, when properly handled, the furnace is capable of producing metal that is as low in phosphorus and sulphur, and as pure and little liable to blowholes, as any steel the world has seen. Hence the process by which the steel is made is, in many cases, of less importance than the skill and knowledge of the workmen, so that the purchaser is better protected by calling for metal of good properties as exhibited by tests than by buying castings made by some particular process that he supposes to be the best. Even electric-furnace steel is subject to this statement. It does not give results, in the ordinary tests, much better than can be obtained with steel well made by some of the other processes; and the growing use of the electric furnace in steel foundries is due as much to the fact that it possesses certain technical advantages for the manufacture of high-grade small castings,

as to the superior excellence of the steel made in it. We know, of course, that electric furnace steel is proving itself superior to other steels, as, for instance, in rails subjected to severe winter weather. But the inevitable uncertainties of steel castings prevent our designing them on as close a margin as we do forgings, so that, as yet, the actual properties of the steel in good steel castings are quite as high as the trade desires. In fact, it is quite possible to make a much better steel than there is a market for.

In general, the open-hearth process, either acid or basic, is the cheapest method for making steel, with the small Bessemer converter next, the electric furnace next, and the crucible process the most expensive. The crucible and Bessemer processes are used mostly for light castings, and the open-hearth for heavier work. The electric furnace, so far, has been used in competition with the Bessemer and crucible processes in making light work, for which it has certain marked advantages. One may hazard a guess that its chief application in the future will be in this field, and that its use for heavy work will be confined to a limited number of cases where steel of very high quality is required.

The most important special steels used in castings are chrome steel, nickel steel and manganese steel. The chrome steel used is generally of a very hard grade, and is furnished for crushing and grinding parts, such as stamp shoes, cement-mill balls, etc. Nickel steel is used in castings for the same reason that it is used in rolled and forged material—because a metal of high tensile strength and elastic limit and of good ductility is required.

Manganese steel is in a class by itself. It is unmachinable, quite strong, very tough, and extremely resistant to wear. It is used to resist almost all sorts of heavy wear and abrasion in crushing and grinding machinery, steam-shovel and dredge parts, railroad frogs and switches, etc.

The general description of the properties of malleable iron found in the first part of this article gives the key to the applications of this material. It is used for a great variety of rather light, and often very intricate, castings in which fair strength and toughness are required. In some applications it has now

been very largely displaced by soft-steel castings; in others, the reverse is true and malleable iron is found displacing steel. Though it is subject to a certain amount of porosity at the center, it is not so liable to blow holes as is steel; and for certain uses it is the best material to buy, despite the fact that its actual strength is not as high as that of steel.

The iron for malleable castings is almost always melted in the air furnace or small open-hearth furnace, as it has been found that the cupola can not be depended upon to give metal of sufficient uniformity to insure successful malleablizing. The composition of the metal has to be kept within quite close limits, which vary in accordance with the size of the castings being made, and the manufacturer has to exercise much skill and ingenuity in designing his patterns and moulds.

The castings are packed in iron boxes, which are heated to a red heat in annealing furnaces of the ordinary type. They are annealed for several days, and test bars or castings in each box are tested in order to be sure that the process has been properly performed.

Specifications for malleable iron usually call for a certain minimum tensile strength and extension on the tensile test, and a minimum transverse strength and angle of deflection on a bending bar. The maximum phosphorus and sulphur content is also often specified.

Cast iron castings, as we have indicated in the first part of this paper, are chiefly used where great strength is not required of the material or where light weight is not necessary, so that the weakness of the material can be allowed for by increasing the size of the sections. There are two general classes of iron castings—plain grey iron and chilled iron. The latter material, as we have already said, is produced by casting grey iron of suitable composition against heavy iron "chills", whereby the part chilled is rendered extremely hard and, incidentally, brittle. The somewhat gradual transition from chilled to grey iron in the casting and the soft grey-iron part of the piece give sufficient strength to the casting, as a whole, to prevent its breaking in service. Of course, a casting chilled all the way through would generally be too brittle to be of any use. Chilled castings are largely used for car wheels; rolls for roll-

ing-mill, paper-making and other machinery; for wearing parts of crushing and grinding machinery; etc.

The metal for high-grade chilled castings is generally melted in the air furnace for the same reason as in the case of making malleable iron,—namely, the fact that close control of the composition of the metal is essential, and this control is easier to secure in the air furnace than in the cupola. The latter furnace, however, is used to a considerable extent for the production of chilled castings.

Plain grey iron may be melted either in the cupola or in the air furnace. The latter is supposed to give a rather stronger metal, and it certainly enables the manufacturer to control the composition of his metal more closely.

There are several varieties of grey iron manufactured under special names, such as "semi-steel", "gun-iron", etc., etc. These metals are not in any sense steel, but are simply high grades of grey-iron; and though their tensile strength is quite high, they possess practically no ductility and should not be used for service where both strength and toughness are essential.

The exact meanings of the terms "semi-steel", "gun-iron", etc., are not yet well established, but the tendency is toward calling air-furnace irons of this sort "gun-iron", and cupola irons "semi-steel". The metal is almost always made by melting from 10 to 40 or 45% of steel scrap with the pig iron, whereby the composition is brought to that which gives the metal the greatest strength for a given size of casting. It should be clearly understood, however, that the identity of the steel, as steel, is wholly lost in the melting and that the metal is in no sense a cross between steel and iron, or a close imitation of steel, but is simply a grey iron, subject to all the limitations of grey iron, and is distinguished chiefly by somewhat greater strength and fineness of grain than is found in ordinary iron castings.

The composition of the iron used for castings of various sizes should be left very largely to the maker, since every element—phosphorus, sulphur, manganese, silicon and carbon—has a very marked effect upon the strength and soundness of the casting; and the composition has to be varied to suit the

size of the work, because the rate of cooling is also a factor of great importance in fixing the qualities of the iron. An iron of very "close" grain, that is, one that shows fine crystals on the fresh fracture, is in a great many cases extremely desirable; the iron must machine freely, etc.

The best way to secure satisfactory castings is to prescribe the tests that the metal must meet—such as strength, ability to withstand a certain hydraulic pressure without developing leaks, machinability, etc.—and leave the composition to the maker, who can generally be depended upon to choose the composition best suited to the requirements. The maximum sulphur, and sometimes phosphorus, content, may be specified, but the engineer should be careful not to go so far in this line as to unnecessarily embarrass the foundryman.

Electric or blow-pipe welding of blow-holes and shrink-holes in steel castings is now a practice recognized in specifications. If the defect is not so located as manifestly to make the casting unfit for use, and if the defect is properly repaired, a welded casting is perfectly satisfactory. The defect, however, should be really eliminated, not simply plugged. By opening a hole to the bottom with the flame or arc, much as a dentist prepares a cavity in a tooth for filling, and then filling it with metal that is welded to the partially fused walls of the hole, the casting can be made truly sound. The hardening effect of the high temperature and rapid cooling upon the steel adjacent to the weld, especially in medium and hard castings, and the stresses set up by the cooling of large welds, make it essential, in a great many cases, that the casting be reannealed after welding. This is especially true if the welded face must be machined.

In general, the problem of making satisfactory castings is so intricate that the purchaser should beware lest he impose impossible conditions upon the foundryman. Specifications should be drawn so that they do not specify both the properties to be obtained and the method of obtaining them. Often, too, a casting is asked for that can not be made successfully at all unless the design is altered. The foundryman becomes, through long experience, an expert in the production of sound castings, and the good engineer should endeavor to cooperate with him

and modify design (and often specifications) in accordance with his suggestions. By so doing he will find, in the majority of cases, that he will secure far stronger and more reliable castings than if he gets on his high horse and refuses to listen to the foundryman, with the result that the latter just does the best he can, and turns out what he knows must be an inferior piece of work which he could greatly improve were his knowledge and skill called into consultation.

Paper No. 165

THE DUPLEX PROCESS OF STEEL MANUFACTURE.

By

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The Duplex Process, in a broad sense, consists of a combination of any two processes. As generally employed in the steel industry it is a combination of the acid Bessemer and the basic open-hearth processes. The acid converter oxidizes the silicon, together with the manganese and a certain portion of the carbon, the exact amount depending upon the practice. The blown metal is then transferred to the basic open-hearth furnace where the phosphorus and the remainder of the carbon are removed.

The Duplex Process shortens the open-hearth purification by more than five-sixths of the usual period, giving a steel of the same quality as the straight open-hearth process.

There are two general methods of operation: In the first method the charge is desiliconized and partially decarbonized in the Bessemer, the remainder of the carbon and the phosphorus being eliminated in the open-hearth furnace. On account of the difficulty in regulating the carbon in the blown metal, this method is not desirable where the amount of phosphorus or other impurities is so low that the duration of the subsequent open-hearth process is determined by the time required to adjust the carbon to the specification limits. In the second method, the charge is desiliconized and the carbon blown down to about 0.10%. The exact amount of carbon desired in the blown metal is obtained by a pig iron addition, made either in the transfer ladle or in the open-hearth furnace, the carbon protecting the metal from excessive oxidation, while the phosphorus is being worked down. This method commends itself on account of the

regularity of the carbon content of the metal going into the open-hearth furnace.

The number of blows required for one duplex heat or one complete open-hearth charge depends on the relative capacities of the converters and the open-hearth furnaces. The usual ratio met with in duplex operation is one to three—three twenty-ton converters supplying sixty-ton open-hearth furnaces with metal, if the three converters are blown at the same time, which is the most efficient method, and the metal assembled in one transfer ladle for removal to the open hearth. Such a Bessemer plant can keep four or five open-hearth furnaces in continuous operation. This is due to the difference in time required by the Bessemer and open-hearth purifications, the former requiring from 15 to 20 minutes, while the latter average from 90 to 110 minutes.

In practice, pig iron is poured into the converters, the blast turned on, and the heats blown, until in the judgment of the blower the metal is of the desired carbon content. In the case of high phosphorus iron, the blow is stopped when the metal contains, approximately, 1.00% carbon; while if the phosphorus is low, the metal is nearly decarbonized. In either case the blown metal together with two or three per cent of lime, to give a basic slag, is charged into an open-hearth furnace; if the metal has been decarbonized, 10% of molten pig iron is added, either in the transfer ladle or in the open-hearth furnace. After the metal is in the furnace an action takes place, the phosphorus oxidizes and enters the slag as phosphate of lime, while the carbon is removed as carbon dioxide. When the phosphorus is within the specified limits, as determined by a rapid laboratory analysis, the heat is tapped and the proper additions for the required manganese and carbon content are made in the steel ladle.

When tapping heats from the open hearth, they may be caught "coming down", or recarburized in the steel ladle. In the first case, the metal is tapped when the carbon content of the bath is within the limits of the specifications of the finished steel, and the manganese in the form of ferro manganese is added in the steel ladle. The disadvantage of the method is that the time required to determine the carbon in the sample is of such duration that by the time the results are known, the metal in

the furnace has not the composition it had when the test was taken; and since the carbon does not drop uniformly, heats are tapped from time to time that do not come within the prescribed limits. When the steel is recarburized in the ladle, the heat is not tapped until it is below 0.20% carbon. In this case, molten spiegel, together with enough iron to give the correct manganese-carbon content in the steel, is poured into the ladle as the heat is run out of the furnace. This method has been found to give the most uniform carbon results in the finished steel.

The loss in the duplex process is greater than that in the straight open-hearth process, but this is largely due to the elimination of carbon, silicon, etc., in the converter, whereas the scrap in the ordinary open-hearth process has already withstood such a loss in its original conversion. To satisfy the slag in the Bessemer conversion, two per cent of metallic iron is oxidized in the converter; this together with a small loss in "shot" and "spittings" is the only loss sustained in the duplex process not common to both processes, working with the same materials.

DISCUSSION

Prof. J. W. Richards,* Mem. A. I. M. E., suggested that a combination of three processes might be used in the same way that two are combined in the Duplex Process. As an example of this, a combination of the Bessemer, open-hearth and electric processes might be used. The Bessemer converter is a great fuel economizer and should not be dispensed with; the open-hearth furnace is useful in keeping heat in the metal between periods of working; while the electric furnace may be used to advantage in the final purification. Prof. Richards.

Mr. H. J. Kennedy inquired if statistics were to be had from any one present concerning the amount of steel at present being made by the Duplex Process. Mr. Kennedy.

Prof. Richards replied that both the Maryland and Bethlehem Steel companies are producing large tonnages. Prof. Richards.

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Paper No. 166

STEEL MAKING IN THE ELECTRIC FURNACE.

By

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Progress in chemistry and metallurgy has kept pace with the world's ever increasing demand for steel, but the instrument with which to apply our knowledge has not always been at hand. At first it was possible to obtain steel-making materials in sufficient quantities and of such purity that steel of fine quality could be made by a simple process requiring little real technical knowledge. As the demand for steel grew, and with it the necessity of lowering the cost, the supply of pure material did not suffice to meet both these conditions. New processes were invented by which steel could be made by the elimination of deleterious elements in the raw material by the use of various chemical reactions. The Acid Bessemer, Acid Open Hearth, Basic Bessemer and Basic Open Hearth processes followed one after the other. Tremendous tonnages were made by these processes, but they did not displace the crucible when the highest grade was required.

All our processes required the application of heat, and all known means of applying heat carried with them oxidizing conditions from which we were not able to protect the material under treatment. We could eliminate objectionable metalloids, and we could add alloys giving various striking and beneficial qualities, but our only means of getting rid of oxygen, for which steel has such a greedy appetite, was by the introduction of materials which had a still greater affinity for oxygen, but which could never grasp the last traces of oxygen, and which left in the steel certain quantities of their own oxides.

Though the oxides in steel are often more deleterious than

moderate quantities of the supposedly more objectionable elements, there has been more or less mystery about them because a ready and practiced every day method of measuring the quantities of these oxides in all the steel we make has not been introduced. But the reason why we did not succeed in making the highest grades of steel in large quantities was because of the lack of an instrument rather than lack of knowledge.

The discovery of the electric furnace gave us the instrument we require to make steel free from all the objectionable elements, including oxygen and sulphur. In this process we use a clean heat. Whether we employ the arc furnace or the induction furnace, the use of kilowatts instead of flame can in no way add oxygen to the metal. Certain elements, as carbon and phosphorus, must first be oxidized before their elimination, and it is necessary to introduce materials, such as iron ore, to give up their oxygen to the elements to be burned. When this is done we can proceed to purify the metal bath from all contaminating oxides, because an overlying slag is supplied which absorbs the oxides, which are in turn broken up, allowing the oxygen to unite with carbon and pass out of the furnace as a gas.

We have in the electric furnace not only a neutral or non-oxidizing condition, but a really reducing condition. We are able to throw sulphur into a basic slag, as in the blast furnace, where the process is one of reduction, but with the conditions existing in the electric furnace we can eliminate the traces of sulphur which cannot be removed in the blast furnace.

Now that the instrument as well as the knowledge has been secured, the use of the electric furnace in steel making must become general unless some still more perfect method is devised, and provided that electric steel can compete with steel made by other processes in cost of production.

The growth in the use of the electric furnace has been rapid, considering that the process is hardly more than ten years old. That upward of one hundred and fifty furnaces have been installed in many different countries shows not only that the interest in the electric furnace is general and widespread, but that many men have invested their money to back their opinions, and they are now getting handsome returns on their investment.

Up to this time installations consisting of units larger than

twenty tons have not been made. When it was demonstrated that electric steel is equal in every way to crucible steel, installations were made with the object of displacing the high grade but expensive crucible steel, and the furnaces used were of a size to conform to the requirements of crucible output.

The reduction in cost of the electric process over the crucible gave a good margin of profit. Experience showed that the better grades of steel, especially alloy steels, which though being made in the open hearth furnace, commanded higher prices than the commoner grades, could be made still better in the electric furnace and with profit. The consumer wished crucible quality, but could not pay crucible price, although able and willing to pay a higher price than that of ordinary basic open hearth. The automobile industry was largely responsible for this demand.

The possibility of adding alloys to the steel, such as vanadium, in the electric furnace without oxidation, and also of melting alloy scrap without any loss of the valuable alloy, often compensates for the cost of operating the electric furnace. The same fact is utilized at a number of Bessemer and open-hearth steel works, where ferro-manganese is melted in an electric furnace and added to the steel in the molten condition. The better deoxidation of the steel in the ladle by the use of molten ferro-manganese greatly improves its quality. At the same time, the loss of ferro-manganese which is experienced when it is placed in the bath in the open hearth furnace or melted in a cupola is avoided.

Electric steel is now being extensively used for such products as tires, axles, seamless tubes and small castings. The fact that electric steel lends itself to heat treatment more readily than other kinds of steel, both as regards greater range of temperature and absence of cracking in the quenched piece, and that there is less loss due to defective material after machining in the machine shop, also gives this steel a preference even at higher prices.

Many have doubted if electric steel can ever be made for such low-priced products as rails and structural material so as to compete with open hearth steel. I believe that the solution of this problem depends upon the adoption of the proper combination process by which the roughing down work will be done by one or several of the older methods using cheap fuel, and the finish-

ing or final refining done in the electric furnace. Both the acid and the basic Bessemer and the open hearth have been used to supply molten metal to the electric furnace. The finishing has been done in both basic and acid electric furnaces.

In the basic electric furnace both dephosphorization and desulphurization can be performed, and it can be supplied with a metal only partially refined, while the acid electric furnace should be supplied with a metal from which both phosporus and sulphur have been removed, requiring greater preliminary refining—going back even to the blast furnace.

During the last two or three years rapid strides have been made with the Duplex or Bessemer-Open Hearth process, and costs are being obtained which compensate for the excessive metal loss in the Bessemer part of the process. It may be that the Duplex process in connection with either the basic or acid electric furnace will give us the solution. However, enough has been already done with the manufacture of the heavier or lower priced products to indicate that, provided it is turned out in producing units of equal size, the total cost of electric steel will be near enough to that of open hearth steel, so that the manufacturer can afford to stand the difference in order to give the consumer quality, the requirements for which are constantly growing more rigid.

The possibility of bringing the cost of the two steels near together will appear more feasible if we consider such incidental savings as the use of cheap pig iron at the beginning of the process and the smaller discard of rolled product due to having an ingot free from segregation.

In Germany, Luxembourg and eastern France, the electric furnace is the best apparent solution of a condition which is a menace to the steel industry of those countries.

While the high phosphorus ores of Luxembourg and Lorraine, together with the basic Bessemer process, made possible the great steel development of Germany, the quality of basic Bessemer steel does not today give it a standing with open-hearth steel, while the demand for better quality is daily growing. On the other hand, basic Bessemer steel, after refining in the electric furnace, is superior to open-hearth steel. The manufacture of electric steel by this method was begun in Germany several years

ago, and has in moderate quantities been made into all kinds of steel products. It seems probable that the American steel manufacturer will find it necessary to adopt electric steel to meet the competition which he will meet in the world's markets.

It has been remarked that the progress of electric steel manufacture in America has been slow as compared with that in Europe, but the indications are that this relation will soon be reversed. It was natural that the invention of the electric furnace should be made in countries where cheap hydro-electric power was already in extensive use for other electro-chemical processes, but it was only a couple of years before the first electric furnace was installed in the United States. We must also remember that the first large furnace, namely, one of fifteen tons capacity, requiring electrodes two feet in diameter, a then unheard of size for steel furnace use, was built here; also that this furnace was the first to use three-phase electric current, which adapted it to utilize the kind of current in general commercial use.

There are now either built or building over forty electric furnaces in America, of which there are twenty-seven of the Heroult type alone. The average size of these furnaces is also greater than the average size in Europe.

If the electric furnace be used for the further refining of steel made in present installations of the older processes, as now seems probable, the amount of electric steel produced should then eventually be commensurate with that now being produced by those processes; and it follows that electric steel production in the United States will exceed that of any other country.

DISCUSSION

Prof. Richards.

Prof. J. W. Richards,** Mem. A. I. M. E., remarked that in the near future, in his opinion, the finishing process in the manufacture of all grades of steel would be conducted in the electric furnace. The possibilities for the extensive development of electric furnace practice on the Pacific Coast of North America were also suggested.

** Lehigh University, So. Bethlehem, Pa.

Paper No. 167

METHODS OF PREVENTING PIPING IN STEEL INGOTS.

By

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In a thoroughly deoxidized steel the freezing or solidification is of the so-called "land-locking" type and depends upon the shape of the horizontal cross-section of the ingot at its various planes from top to bottom, and also upon the heat absorptive quality of the mold and the degree of the so-called "lag" in freezing of the steel.

When thoroughly deoxidized, the liquid steel as it is poured into the mold has a volume of approximately 6% greater than in the solidified ingot, and as the outer portion of the ingot necessarily cools or solidifies first, a void obviously occurs in some portion of the ingot during the process of solidification. To force this cavity or the unsound material surrounding the same to the upper portion of the ingot must be the primary object of all successful pipe reducing devices.

Sir Robert Hadfield's methods* of utilizing a blow pipe in conjunction with a supply of charcoal placed within a refractory sink-head into which the upper portion of the molten steel of the ingot extends, unquestionably locates the piped or unsound material at the extreme top of the ingot. The author has examined split "Hadfield" ingots which have been sent to this country and which had less than 5 per cent of piped material.

Mr. E. F. Kenney has recently proposed a special form of combined metal and refractory material sink-head, which, when used with big-end-up molds, produces most excellent results,† the novelty of the Kenney design being in the combination of a refractory and a metallic sink-head, the proposition being to

*British Iron & Steel Institute, September, 1912.

†American Iron & Steel Institute, May, 1915.

strip the ingot from the mold with the refractory sink-head remaining on the ingot. The stripping can thus be accomplished much earlier than is possible by Hadfield's method, thus utilizing to a large degree the initial heat of the ingot and requiring less time in the re-heating pits preparatory to working of the steel.

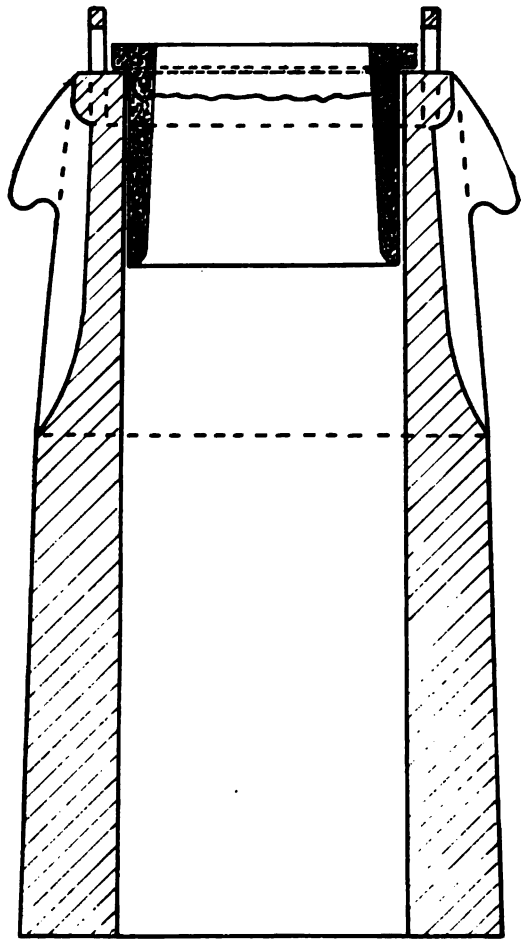
How to accomplish the reduction of pipe in a commercial manner at a minimum expense and without upsetting the administrative mill practice of present plants is the problem.

An ingot with its larger horizontal cross-sectional area at the top is without question the best shape for obtaining the important so-called "lag" in freezing or solidification of the steel, and whenever such large-end-up ingots can be conveniently used, it is the best practice to do so.

The writer has proposed a method‡ which he believes will solve the problem, and which is at the present time being installed at one of the works of the United States Steel Corporation, but is, however, still in an experimental stage and can, therefore, not as yet be considered in the commercial production of sound steel. Nearly all of our large mills are so equipped in an administrative way of handling and stripping of the ingots from the molds that it is practically impossible to utilize big-end-up practice without extensive changes in equipment. This is especially true in the production of rail steels where tonnage must be produced in order not to incur prohibitive expense which might offset any advantage obtained by lessened crop. The writer employs means in ordinary big-end-down ingots to greatly accelerate the freezing or solidifying of the lower or body portion of the ingot, and by increased differential or lag in cooling of the upper portion of the ingot providing liquid metal to supply uninterrupted feeding to compensate for the decrease in volume caused by the contraction of the feeding or solidification of the lower and body portion of the ingot. This has been accomplished by giving the lower 70 or 80 per cent of the metallic mold in which the ingot is cast a much greater degree of heat absorptive quality than the upper 30 or 20 per cent thereof. This construction will be best understood by referring to the annexed drawing. This type of mold is in daily

‡American Institute of Mining Engineers, February, 1913.

use under usual furnace and mill conditions at a number of large steel plants, hundreds of thousands of tons of steel having been made by this method.



A mold with heavy lower body walls and thin upper walls, *per se*, properly designed, will produce a sound homogeneous ingot with about a 20 per cent top crop in split ingots of dead killed steel, which is about 15 per cent less than is usually necessary in cropping cold ingots made in the old type of mold of like grade of steel.

The theoretically ideal method of making sound homogeneous steel with a minimum crop, to rid same of segregation and piped section, is undoubtedly with the big-end-up mold—as proposed by Professor Howe, Sir Robert Hadfield, Mr. Kenney, the writer and others—as the increasingly large area of the ingot towards the top compensates automatically for any irregularities in the heat of steel and teeming practice.

In the commercial production of sound ingots and blooms, tonnage and quality must, however, be jointly taken into consideration; and this being the case, it will be some time, in the writer's opinion, before the big-end-up displaces the big-end-down type of mold, except for special grades of steel. The big-end-down mold with heavy-walled body, light-walled top and fitted with a suitable sink-head or feeder certainly gives a tremendous advance in the assurance of sound material and lessened crop, as compared to the ordinary method of casting. Reports from mills using these methods show that a very considerable saving has been effected and that good steel is made better in all cases where the molten steel, *per se,* has been made sound by thorough degasification, which latter is without question the first essential requisite for the production of sound homogeneous steel, be it by the Hadfield, Kenney's, the author's, or any other method.

DISCUSSION

Prof. Lawson.

Prof. A. C. Lawson,* Mem. A. I. M. E., inquired whether qualified observers had ever noted any peculiarities in the crystallization of the incrustations found on the inside of voids left in iron and steel castings.

Prof. Richards.

Prof. J. W. Richards,** Mem. A. I. M. E., replied that the crystallization of these incrustations had been noted by several observers and that specimens were to be seen in several mineralogical museums.

He doubted if many steel makers would agree that it is best to completely deoxidize or "kill" the metal before casting, as he claimed that steel makers usually prefer a partially deoxidized metal so that a few small blow-holes, which are of some advantage in the subsequent rolling process, will be left in the casting. He agreed, however, with Mr. Gathmann that the best method is to completely deoxidize the steel, relying on improved methods of casting to overcome piping.

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** Lehigh University, So. Bethlehem, Pa.

Mr. Eaton.

Mr. G. M. Eaton,*** Mem. A. I. E. E., inquired if there were not danger, in the proposed method of casting, of weakening the metal in the lower part of the ingot at the junction of the completely deoxidized and partially deoxidized metal.

Mr. Parmelee.

Mr. H. C. Parmelee**** inquired if any physical change of segregation of the constituents could be noted as a result of piping. He said that within his experience an examination of samples taken from different portions of a defective steel rail showed from two to three times as much sulphur and phosphorus in the head of the rail as in the web.

Prof. Richards.

Professor Richards replied that it was quite unlikely that the steel was a "dead" steel which would pipe readily.

Mr. Eaton.

Mr. Eaton said that he had knowledge of a series of different portions of a large ingot which had been completely deoxidized before casting, and that samples from different parts of the ingot showed no segregation of the constituents.

Mr. Beckman.

Mr. J. W. Beckman* inquired as to the nature of the insulating material used in Gathmann's process of casting.

Prof. Richards.

Professor Richards replied that it must have been fire clay, and that the clay must necessarily go to waste when the ingot is "cropped".

*** Pittsburgh, Pa.

**** Denver, Colo.

* San Francisco, Calif.

Paper No. 168

ALLOY STEELS.

By

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Steel can broadly be defined as an alloy of iron and carbon that can be forged and rolled. From expediency and necessities of manufacture, certain impurities beneficial or otherwise are present, but not in sufficient amounts to materially alter the characteristics of the pure alloy of iron and carbon.

Under this definition, steel, or as it is now often referred to, carbon steel, is usually within the following maximum composition:

Carbon, 1.50%.
Manganese, 1.00%.
Silicon, 0.35%.
Phosphorus, 0.05%.
Sulphur, 0.05%.

An "alloy" steel is steel alloyed with one or more metals, in sufficient amounts to influence or change the characteristics of steel, and still possible of forging or rolling.

The usual steel alloying metals are Manganese, Silicon, Nickel, Chromium, Tungsten and Vanadium. As these metals will all alloy with each other, it is evident that it is possible to obtain a great variety of alloy steels.

Steel containing upwards of 1.50% manganese is not commonly considered an alloy steel, although this percentage of manganese undoubtedly has some effect on the characteristics of steel. This is due no doubt to the fact that manganese is always present in steel.

The alloy steels are usually divided into two groups: "ter-

nary'' steels, with one metal alloyed, and ''quarternary'' steels, with two metals alloyed. The more complex alloy steels are practically limited to high-speed tool steels.

The general characteristics of alloy steels are high elastic limit and great strength, combined with a high degree of toughness as compared with the carbon steel with which they are alloyed. The strength and hardness can be enormously increased by heat-treatment (quenching and tempering) and still have the steel retain great toughness.

Alloy steels are not as a rule placed in service in the condition as forged or rolled. The forging and rolling temperatures are usually so high that the steel requires heat-treatment to refine the grain and develop the exact combination of strength, hardness and toughness desired. It is frequently necessary to anneal after forging in order to facilitate machining operations. This, of course, necessitates subsequent heat-treatment.

Most of the alloy steels are of medium or low carbon content. The corresponding simple or carbon steels are only slightly or moderately improved in strength by heat-treatment.

The use of alloy steels in cutting tools dates back nearly a hundred years, although it was not until after 1850 or 1860 that alloy steels for this purpose became firmly established.

With the advent of iron-clad warships began the struggle for supremacy between projectile and armor plate that has been so fruitful in the development of alloy steels. Chromium, nickel and nickel-chromium steels are largely the result of this struggle.

The publication in 1888 by Hadfield of the results of an extensive research of the alloys of manganese and steel, which resulted in the discovery of a remarkable new alloy steel, marks a period of active investigation into the effect of other metals on steel. The most important of these were the investigations on nickel steels by Jas. Riley in 1889, which demonstrated that a mild open-hearth steel, such as used for structural, general forging and machinery purposes, when alloyed with 3% to 4% nickel had considerably higher elastic limit and tensile strength, with practically the same or greater ductility. One of the earliest and most extensive applications of nickel steel was for armor plate. For many years nickel steel was the principal alloy steel in use.

During this same period referred to, Hadfield made investigation of the effects of silicon on steel, and also a very complete study of chromium steels, which for some time had been used in a small way for springs and special forgings, but principally for tools and armor-piercing projectiles.

The development of high-speed steel about 1900, making it possible to readily machine heat-treated alloy steels, and the advent of the automobile with its demand for superior steel, have brought about the present extensive use and development of alloy steels.

The automobile industry, with its demand for steel of high strength and durability, has been undoubtedly the most important factor in the development of commercial alloy steels, and the largest consumer. Alloy steels are used extensively for transmission gears and shafting, axles, steering levers and spindles, springs, chassis frames, crank shafts, cam shafts, connecting rods, valves and many other parts of automobiles.

They are also extensively employed in forgings for high-speed engines, marine engines, locomotives, electrical machinery, mining machinery and other mechanical engineering structures.

The use of alloy steels in bridge construction has been limited, but there is undoubtedly a field in long-span bridges for an alloy steel of high strength that can be used in the condition as rolled, preferably, or at most with a simple annealing.

Coincident and having a marked influence on the development of alloy steels, was the discovery of large deposits of vanadium ore in Peru, thus assuring a source of supply at a reasonable cost of this rare metal, which is the most powerful yet discovered for alloying with steel, that is, in small amounts.

The most important of the engineering or constructural alloy steels are those containing nickel, chromium and vanadium, singly or in combination. With all these steels it is possible, through heat-treatment, to obtain a tremendous range in strength, in round numbers varying from 100,000 to 250,000 pounds per square inch, depending also, of course, upon the size of the section.

It is not possible nor within the province of this paper to go deeply into the technology of alloy steels, but only to briefly describe the principal alloy steels and their characteristics.

Manganese Steel.

This steel usually contains 10% to 13% of manganese and approximately 1% of carbon. It is practically non-magnetic and has a peculiar hardness to which it owes a remarkable resistance to abrasion. It is extremely difficult to machine. It has high strength and toughness, but relatively low elastic limit. With care it can be forged and rolled. It has found its principal application in castings for crushing and grinding machinery and railroad crossings. Manganese steel has the peculiar property of being toughened and softened by quenching in water, resembling copper in this respect. All manganese steel castings are subjected to this treatment to remove brittleness.

Silicon Steel.

There are two types of silicon steel, one of which has found some application as an engineering steel. This steel, frequently called silico-manganese steel, is generally covered by the following limits of composition:

Carbon, 0.45% to 0.65%,
Silicon, 1.50% to 2.00%,
Manganese, 0.50% to 0.80%;

the manganese is normal, contrary to what is indicated by the name. The principal application of this steel is for automobile springs, and to some extent for gears. It fibers readily through heat-treatment, and is very brittle in the direction at right angles to rolling. It is very sensitive to heat-treatment, and a relatively small variation in annealing temperature after quenching has a strong effect on the results obtained.

The other type of silicon steel contains 3% to 5% silicon, is low in carbon and manganese and is extensively used for electrical transformer sheets on account of its high permeability and electrical resistance. Structurally, it is weak and has no constructural value.

Nickel Steel.

Nickel alloys with steel in all proportions, but by far the most important nickel steel, from an engineering standpoint, is the low- and medium-carbon steel with 3% to 4% of nickel, commonly known as 3½% nickel steel. The presence of manganese in nickel steel is very essential, as it has a marked effect on the

mechanical properties. The amount of manganese should range from 0.50% to 0.80%. This steel has been extensively used since its introduction in 1889, and is a good all-round engineering and structural steel with considerably higher elastic limit and tensile strength than the corresponding carbon steel, and with practically the same degree of ductility. The low-carbon steel, 0.10% to 0.20% carbon, is used extensively for case-hardening parts. It case-hardens more readily than carbon steel and gives a harder casing with a strong, tough, fibrous core. A great deal of nickel steel with carbon from 0.20% to 0.35% has been used in shapes and plates as rolled, and in annealed eye-bars for bridge construction. In this condition, which is not to be recommended for forgings, the following are typical physical properties:

Elastic limit, lbs. per sq. in.	45,000 to 60,000
Tensile strength, lbs. per sq. in.	80,000 to 100,000
Elongation in 2 inches, percent.	20% to 15%
Reduction of area, percent.	40% to 25%

Annealed nickel steel forgings have only slight advantage in strength over carbon steel, and consequently are not advantageous, either from an engineering standpoint or commercially, unless heat-treated. With heat-treatment it gives considerably higher strength than carbon steel, combined with greater ductility or toughness. It does not give as high values as the nickel-chromium and chromium-vanadium steels. Nickel steel rolls and forges readily and machines easily. It develops a very thick, hard scale which is apt to give considerable trouble in drop-forging and is hard on the dies. Nickel steel is also very liable to develop seaminess, especially when made in large heats and cast into large ingots, as is now customary. It requires a larger discard to ensure soundness. The use of nickel steel in forgings, and particularly drop-forgings, is falling off in favor of other alloy steels with greater values.

Chromium Steel.

The use of this steel is confined principally to a few specialties and it is not in general use as an all-round engineering steel. One of the principal uses is for balls and ball races. The great mineralogical hardness obtained by quenching is very desirable for this purpose. The steel for this application contains approximately 1% each of carbon and chromium.

Chromium steel is also used for stamp-mill shoes, and in combination with soft steel in laminated plates for construction of burglar-proof safes, and in the same combination in bars for jails.

The low- and medium-carbon types, containing 0.80% or less of chromium, have somewhat higher mechanical properties than the corresponding carbon steel. They are not used to any great extent, other alloy steels being superior, both in static and dynamic strength. Chromium steel is also very liable to crack and check in heat-treatment.

Nickel-Chromium Steel.

The addition of chromium to nickel steel has a marked effect, greatly increasing the strength and resistance to shock and particularly the mineralogical hardness. It is more difficult to forge and heat-treat and harder to machine, and is also liable to the seaminess frequently present in nickel steel. There are three types of this steel, differing both in the percentage of nickel and chromium, and all with low or medium carbon:

	Nickel	Chromium	Carbon
1st	3.5%	1.50%	0.25% to 0.45%
2nd	2.0%	1.00%	0.10% to 0.45%
3rd	1.5%	0.50%	0.10% to 0.45%

The first type is used principally for armor plate and armor-piercing projectiles and came into use about 1895, superseding the nickel plates and chromium projectiles. The other two types were developed by the automobile industry. The second type is used largely for automobile forgings. It gives high strength with heat-treatment, has great hardness and good shock- and fatigue-resisting qualities. The third type is a largely-used, all-round engineering steel. It is used for automobile forgings and for a variety of miscellaneous drop-forgings and machine parts. It is an excellent case-hardening steel, carbonizing readily. This type is more tractable in working, heat-treating and machining than the other two. It is also somewhat lower in tensile strength.

Vanadium Steel.

The addition of small amounts of vanadium, generally under 0.25%, to simple carbon steel or any of the alloy steels increases very considerably—about 30% or more—the elastic limit and

breaking strength, without materially affecting the ductility. To an even greater extent it increases the resistance to shock and fatigue.

The vanadium steel which has been up to now most generally used is a chromium-vanadium steel of the following typical composition:

Carbon, 0.10% to 0.55%.
Manganese, 0.50% to 0.80%.
Chromium, 0.80% to 1.00%.
Vanadium, over 0.15%.

The lower carbon type, 0.10% to 0.20%, is used mainly for case-hardening and is the best steel for this purpose. It carbonizes readily, gives the highest maximum carbon and finest grain. The casing is very strongly coherent to the core, very hard, tough and strong and practically free from any tendency to flake or powder. The core is remarkably strong and tough.

The higher limits of carbon, 0.45% to 0.55%, are extensively used for automobile and locomotive springs, giving remarkable resiliency and endurance. They are also extensively used for oil-tempered gears.

The range in carbon from 0.35% to 0.45% is largely employed for crank shafts, locomotive axles, crank pins, connecting rods, hammer piston rods, automobile transmissions and rear-axle shafts.

The range from 0.25% to 0.35% carbon is used for automobile forgings of all kinds and a great variety of miscellaneous work requiring the best combination of static and dynamic strength.

As illustrating the wonderful shock and fatigue enduring qualities of chrome-vanadium steel, drop-hammer piston rods of this material are giving many times the length of service of carbon, nickel and chromium-nickel steel rods.

Vanadium steels have a much wider heat-treatment range than other steels. The desired physical properties can be obtained with a higher draw-back or annealing temperature, which is very advantageous as more completely removing quenching strains, and also as a manufacturing proposition.

Chromium-vanadium steel forges and machines better than nickel-chromium steel, is not as liable to injury in heating for forging, is not so liable to crack or check in heat-treatment and is free from the seamy tendency of steel containing nickel.

Carbon steel with a small percentage of vanadium, from 0.15% to 0.20%, has been used extensively for locomotive-frame castings with great success. The failures of these frames from all causes over a period of nearly ten years has been only a fraction of one percent.

In tool-steel grades, this steel has better cutting qualities, hardens deeper and more uniformly, and has remarkable toughness. In what are termed battering tools, chisels, cutters, dies, etc., it gives several times the length of service of ordinary carbon tool steel.

The handicap of high cost of vanadium has almost disappeared, and simple carbon-vanadium steel in the ordinary forging grades will undoubtedly soon become very widely used as an all-round engineering steel, when a better steel than carbon is required. It is remarkably clean and is as easily worked as carbon steel. It is free from the seaminess and ugly scale of nickel steels and the tendency to check and crack of the chromium steels, particularly nickel-chromium.

Tests are showing about 20% less wear for carbon-vanadium steel rails in curves than for rails with 0.15% to 0.20% higher carbon, and they are also considerably stronger. This difference in wear will doubtless be much greater when the carbon percentage in the vanadium rails is increased to that of the standard rails.

In simple annealed forgings, plain vanadium steel has physical properties well above those specified for heat-treated (quenched and tempered) carbon steel.

This type of vanadium steel has a wider range of quenching temperature than nickel or nickel-chromium steels; and for mechanical properties after heat-treatment is practically on an equality with 3½% nickel or the low nickel-chromium steels in general use, and apparently has higher fatigue resisting qualities.

While nickel and chromium interfere seriously with the welding quality of steel, vanadium does not, but on the contrary improves this quality. Vanadium steel wire is in common use for autogenous welding.

Tungsten Steel.

This is principally used for magnets for magnetos and to some extent in hack saws and special tool steels. Tungsten is seldom used in engineering constructional steels, and then usually in combination with chromium.

The following table shows the typical engineering alloy steels and their tensile properties for the same heat-treatment draw-back temperature. This is in all cases 600 degrees Centigrade (about 1100 degrees Fahrenheit). The specimens in most cases were heat-treated in the form of inch rounds and were machined after treatment.

Carbon %	Manganese %	Nickel %	Chromium %	Vanadium %	Elastic Limit Lbs. per sq. in.	Tensile Strength Lbs. per sq. in.	Elongation in 2 in. Percent	Reduction of Area Percent
.27	.55	.....	.....	....	49,000	80,000	30	65
.27	.47	.....	.....	.26	66,000	98,000	25	52
.36	.42	.....	.....	....	58,000	90,000	27	60
.34	.87	.....	.....	.13	82,500	103,000	22	57
.45	.50	.....	.....	....	65,000	96,000	22	52
.43	.60	.....	.....	.32	96,000	122,000	21	52
.47	.90	.....	.....	.15	102,000	127,500	23	58
.30	.60	3.40	.....	....	75,000	105,000	25	67
.33	.63	3.60	.....	.25	118,000	142,000	17	57
.30	.49	3.60	1.70	....	119,000	149,500	21	60
.25	.47	3.47	1.60	.15	139,000	170,000	18	53
.25	.50	2.00	1.00	....	102,000	124,000	25	70
.38	.30	2.08	1.16	....	120,000	134,000	20	57
.42	.22	2.14	1.27	.26	145,000	161,500	16	53
.36	.61	1.46	.64	....	117,600	132,500	16	58
.36	.50	1.30	.75	.16	140,000	157,500	17	54
.30	.50	.....	.80	....	90,000	105,000	20	50
.23	.58	.....	.82	.17	106,000	124,000	21	66
.26	.48	.....	.92	.20	112,000	137,000	20	61
.35	.64	.....	1.03	.22	132,500	149,500	16	54
.50	.92	.....	1.02	.20	170,000	186,000	15	45

Complex Alloy Steel.

Practically none of the constructional steels contain three or more alloy metals. The only steel in this class to be considered is what is commonly known as high-speed steel. Robert

Mushet developed and patented about 1860 an air-hardening steel that was very much superior to carbon tool steel for machining hard material. Mushet steel, as it was known, had about the following composition:

Carbon, 2.00%.
Manganese, 1.75%.
Silicon, 0.75%.
Chromium, 0.40%.
Tungsten, 5.50%.

At the Paris Exposition in 1900, the Bethlehem Steel Company exhibited a new tool steel that took wonderfully heavy cuts at high speeds, the point of the tool heating up to a strong blue color without losing its edge. This steel, which immediately became known as high-speed steel, was the culmination of the research work carried on for many years by Mr. F. W. Taylor and later published in his monograph "The Art of Cutting Metals". The difference between this steel and Mushet steel is apparent from the following typical composition:

Carbon, 0.60%.
Manganese, 0.20%.
Silicon, 0.10%.
Chromium, 4.00%.
Tungsten, 18.00%.

With this steel, cutting speeds of over 90 feet per minute were obtained.

Within three or four years it was found that the addition of vanadium to high-speed steel made it possible to still greatly increase the speed and size of cut. At first only about 0.30% vanadium was added, but this has been increased until now 1.00% is practically the standard amount in most high-speed steels, and speeds of 140 feet and upward per minute have been attained.

Lately the addition of cobalt to high-speed steel has been meeting with favor as still further improving the endurance of the steel. The amount of cobalt generally used is 3% to 4%, with no change in the percentage of the other metals—tungsten, chromium and vanadium.

DISCUSSION

Prof. Richards. **Prof. J. W. Richards,*** Mem. A. I. M. E., remarked that it may be interesting to note under the discussion of high-speed steel that Mr. Haynes of Indiana is the inventor of an alloy, which contains no iron whatever, that is said to be superior to some of the best high-speed tool steels.

Mr. Eaton. **Mr. G. M. Eaton,**** Mem. A. I. E. E., inquired whether the copper in Mr. Haynes' alloy was responsible for its toughness.

Mr. Kennedy. **Mr. H. J. Kennedy** inquired as to what was the dominant metal in Haynes' alloy, and the price per pound.

Prof. Richards. **Professor Richards** replied that a recent analysis showed the alloy to contain: Cobalt 52.03%, chromium 29.36%, tungsten 12.71%, iron 5.35%, nickel 0.45%, manganese 0.24%, silicon 0.09%, molybdenum, trace. The commercial name is "stellite".

Mr. Norris. **Mr. G. L. Norris,** in closing, said that he would like to add to what Professor Richards has said about stellite, that vanadium also enters into its composition.

As to high-speed tool steel, it is interesting to note that on account of the present scarcity and very high price of tungsten, there is a growing tendency to increase the percentage of vanadium and lower the percentage of tungsten in this class of steel. Some makers have reduced the tungsten 30% to 50% and increased the vanadium over 100%, so that now 2% to 3% of vanadium is not uncommon. These high vanadium, high-speed steels have been demonstrated in every way equal, and usually superior, to those containing the higher (18%) percent of tungsten.

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Paper No. 169

THE RECENT PROGRESS AND PRESENT STATE OF THE TECHNICAL APPLICATION OF THE CASE-HARDENING OF STEEL

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INTRODUCTION.

(1) It is very frequent in the practice of mechanical construction to meet with cases in which a given piece of metal must satisfy at the same time two fundamental conditions, in a certain sense in antithesis one with the other—as for example on one hand the condition of possessing a very high superficial hardness such as to render it suited to resist in the best possible manner the wear produced by rubbing attrition, and on the other hand the condition of presenting in the body of the substance a tensile strength sufficient to render it suited to resist effectively the action of alternating forces or of shocks.

Aside from the construction of parts of machines or of tools destined to the cutting of metals, there is presented also in certain other cases—such as for example that of the fabrication of armor plates—the necessity of obtaining an extreme hardness in one part of a piece of steel which, in the remaining parts, should possess the highest possible tensile strength.

(2) I have said that the two conditions noted above are in a certain sense in antithesis one in respect to the other, and this by reason of the fact, well known, that steels possessing the highest resistance to scratching or cutting and therefore the best suited to resist wearing by abrasion, are generally also the most brittle and therefore the least adapted to resist the action of alternating forces or of shocks. It is indeed true that this last

fact is greatly modified in various types of special steels, introduced recently into technology, such that some of these steels (for example certain manganese steels) after having undergone suitable heat treatment, present a high resistance to abrasion joined to a tensile strength sufficient for all principal mechanical applications. However, in such steels these two qualities are likely to be coupled—in greater or lesser measure—with two inconveniences which seriously limit their practical application. The first of such inconveniences consists in the high price. The second is found in the serious difficulty of suitably softening these steels through heat treatment in such manner as to render them susceptible to attack by the cutting tools with which they are to be fabricated. It follows that the mechanical working of all parts made of such steels is always extremely expensive.

(3) Now, it is known that, among all the elements which may enter into the composition of the various types of steel best suited to the construction of mechanical parts, carbon is that whose variations of concentration give rise to the most pronounced variations in the hardness of the steel after quenching; and in the sense that—with all other conditions equal—the surface hardness of a steel belonging to one of the types noted above increases in marked degree (after quenching) when its content of carbon undergoes an increase, also when the increase of the carbon content is relatively small. However, in conjunction with a marked augment in the surface hardness, slight increase in the carbon content gives rise to the most marked increase in brittleness in the quenched steel. It results that whenever it is desired to construct a mechanical member of homogeneous steel with high resistance to abrasion, without at the same time being able to yield largely the requirement of strength to resist shocks or alternating stresses, it cannot be expected to realize the desired result simply by increase in the carbon content of the steel throughout the entire mass employed. As I have already pointed out for this case, when it is desired to use a homogeneous steel, it is necessary to have recourse to the introduction of new metallic elements in the steel (for example chromium, tungsten, etc.), or to an increase in the content of those already present (as manganese for example). There are thus obtained special steels, of which I have made note just above. These, aside from pre-

senting the serious practical drawbacks which I have already noted and which render them poorly adapted to mechanical construction, do not permit of realizing, in the way of surface hardness, values as high as those which may be obtained with quenched steel containing a high carbon content.

(4) All the advantages of the high surface hardness obtainable in quenched high carbon steel, may, on the other hand, be obtained—and without renouncing strength to withstand shocks or alternating stress—by abandoning the concept of imparting to the entire mass of the piece the two antithetical properties noted above and seeking to develop each one of them in dominant degree and to the highest possible extent, only however, in those parts of the piece in which it is definitely useful.

In fact it is clear that in the greater number of cases, it is quite sufficient if the hardness necessary to impart to the piece a high resistance to abrasion, is found in a surface layer of the member; while on the other hand, the necessary resistance to alternating stress or to shock can be obtained only on condition that the greatest possible part of the metal of which it is formed possesses a high tensile strength. It therefore readily appears rational, in all cases in which, in a single mechanical member the two characteristics noted above are required in high degree, that use should be made of a material in which a superficial zone, more or less deep, shall present the highest practicable resistance to abrasion (even at the expense of some sacrifice, in even notable degree, of the tensile strength), while on the other hand the main body of the member should be made of a material with high tensile strength, suited to effectively resist alternating stresses or shock, and with just the degree of hardness which is strictly necessary in order to constitute an effective support for the hardened layer which rests upon it.

Such conditions are in fact satisfied in the best manner when use is made of parts fabricated from soft steel subjected to a superficial cementation or case-hardening process, carried to a suitable depth and followed by a suitable heat treatment.

(5) As is well known, the general process of cementation consists in heating (for a longer or shorter time) the piece of steel to be treated, at a temperature above the first point of transformation by heat for the steel under treatment, but always

much below its point of fusion, while maintaining the surface in intimate contact with substances capable of decomposition—under the existing conditions—with liberation of carbon.

When a suitable choice has been made of the carburizing substance and of the conditions under which the operation is carried out, there is then realized a process of diffusion of the carbon, liberated from the carburizing substance, into the mass of the steel. In this manner, the operation being completed, the metal constituting a layer of the steel lying immediately below the surface exposed to the treatment will have absorbed a certain quantity of carbon depending on the duration of the operation and on the conditions (especially temperature) under which it has been carried out. The thickness of the layer thus carburized and the variation of concentration of the carbon in its various parts, depend closely on the nature of the carburizing substance used and on the conditions under which the process has been carried out. It may, however, be stated that the concentration of the carbon in the stratum carburized, decreases in general (although not always in uniform manner) in passing from the layers nearer the surface to those lying at greater depth, until finally and gradually, at a certain depth, the initial value for the untreated steel is found.

However in special cases—which in modern metallurgical practice become ever less frequent—the process is carried to the point of raising in marked degree the concentration of the carbon in the entire mass subjected to treatment.

Being given the characteristics, above noted, of a piece of mild steel subjected to a superficial cementation (case hardening), it is almost always possible to choose a heat treatment suited to confer on the external carburized surface, a very high degree of hardness by way of resistance to abrasion, and to the heart of the mass of metal lying below the surface, not subjected to carburization, a high degree of tensile strength. Such heat treatment—brief reference to which will be made at a later point—normally consists of one or more operations of quenching.

(6) The process of partial cementation of objects of iron—employed for the purpose of partially transforming them into steel capable of being hardened—seems to have been known since very ancient times. But the first clear account of a proc-

ess which might be considered as a genuine process of cementation, seems to be that contained in the works of Vannuccio Biringuccio, a native of Siena, and published in 1540 under the title of "*Pirotechnia*". The process described by Biringuccio is, however, a process of complete cementation through the entire mass of iron.

The history of the development of both the science and the art relating to the process of the cementation or case hardening of steel and to its technical applications is very interesting, but space is lacking to here refer to this phase of the subject, even in summary form. For this purpose, I must therefore refer to the works mentioned in the bibliographical index accompanying herewith. I cannot, however, do less than note the fact that—while in a first and very remote period of time, which it appears might reach back to the first years of the Roman empire and which extends forward to the end of the 16th century, the process of case hardening was used commonly for the partial transformation into steel, of objects in iron after being completely formed—in a later period the importance of such application of cementation was in great measure superseded by the importance assumed by the other form of application of the same process, consisting in the complete carburization of masses of iron in order to transform them into hard steel, of composition approximately uniform throughout their mass, and from which, by suitable thermal and mechanical operations, various objects of steel may be made. Such process received even wider usage, especially after the classical researches of Réaumur (1720-1722), which threw greater light on the details of the phenomena on which the process of cementation depends, and after the English horologist Benjamin Huntsman (1740) had discovered, and later reduced to practical application on a large scale, the process of the melting of steel in a crucible, thus creating a great new industry, of which the principal raw material was in fact iron in bars, completely carburized by cementation.

Finally, in a third period of time, which may be taken as counting from the middle of the 19th century and which reaches down to our own days, there has developed in the industry of the cementation of steel, a reversion, as a result of which the industry itself has turned back to the characteristics of earlier

years. In fact, while on the one hand improvement in the technique of mechanical construction was placing on the metallurgists, with ever increasing frequency, problems, the natural solution of which was represented by the use of parts subjected to superficial cementation—on the other hand the introduction of new methods of steel-making (Bessemer, Thomas, Siemens-Martin, electro-thermic) made possible the provision, at a much reduced cost, of the very best material, and capable of replacing in most cases the product previously obtained only through the use of iron completely carburized by the cementation process. The effect of this evolution was a decrease in the importance of the industry of steel-making by the complete cementation of iron (an industry which today is of quite secondary importance) and a gradual though pronounced growth in the importance and in the diffusion of the application of the process of partial or superficial cementation (case-hardening) especially for the fabrication of various machine elements and parts.

(7) This being understood, I propose to develop forthwith, in the extremely summary form which is imposed on me by the limitations of space, some of the most important points concerning our present theoretical knowledge of the process of case-hardening, and the conditions under which such process is today most frequently applied in the arts.

CHAPTER I.

PRESENT CONDITION OF THE THEORETICAL KNOWLEDGE CONCERNING THE PROCESS OF CASE-HARDENING OF STEEL.

(8) The problems most frequently discussed among those who are interested in the theory of cementation are two.

The first is that which has for its object to determine whether the passage of the carbon from the carburizing substance to the superficial layer of the steel consists in a simple phenomenon of solution of the solid carbon in the iron, with the surface of which the carburizing substance is placed in contact. Such an explanation of the process would not be unnatural, because at the temperature of the cementation process the iron is found in the gamma state with which carbon readily

forms solid solutions. And furthermore, many examples are known of solid bodies which, placed in contact with the surface of other solid bodies, penetrate and form a solid solution, and without the possibility of the intervention of gaseous substances. Such condition, for example, is met with in the case of lead placed in contact with gold.

In cases where the carburizing substance employed is a compound containing carbon, and in the solid or liquid state (a cyanide for example) or where it is gaseous (generally a hydrocarbon) the partizans of the hypothesis above noted (of the direct action of the solid carbon) assume that the action is carried on by the effect of the carbon which the composite body—undergoing decomposition at the high temperature of the cementation process—deposits on the surface of the piece of steel.

In place of this hypothesis, sustained moreover through the past by various experimenters (although in truth by means of experiments not always carried out with the necessary rigor) many on the other hand urge another, which—excluding entirely the possibility of a phenomenon of direct solution of carbon in iron—explains the passage of the carbon from the carburizing substance to the superficial layers of the steel, solely by the action of carbon bearing vapors or gases (cyanogen, carbon monoxide, hydrocarbons, etc.), which—even in the case where a solid carburizing substance is employed—are always present in the atmosphere which impregnates the mass of the substance. Such a gas, diffusing itself (by a process which, moreover, may be directly noted in many other cases) and thus penetrating into the mass of the steel, is there decomposed and yields to the metal a part of its carbon.

The second of the problems noted above is closely related to the first. It is concerned with the question of whether the phenomenon of diffusion of carbon from the superficial layers to those deeper and deeper, in the case of a piece subjected to cementation, is realized as a result of the difference in concentration of the solid solution of carbon and iron which constitutes the layers themselves, or whether it is due to a diffusion, in the mass of the metal, of vapors or carburizing gases, the which, undergoing gradual decomposition, yield up a part of their carbon to the steel of the successive layers.

(9) The two problems above indicated have given rise to heated discussions, beginning in the first half of the 19th century and not altogether exhausted even at the present day.

Unable here to indicate, even briefly, the points of these most interesting and instructive discussions, I must be content with indicating summarily the conclusions to which the most recent and presumably the most reliable experiments seem necessarily to lead.

It is desirable to premise that the carburizing substances now used most frequently—either mixed together or with some other substance or used alone—may be classified under the following groups:

(a) The varying types of coal, as used in the arts, and in which the predominating element is carbon. Such are, for example, wood charcoal, fossil coal, soot, bone black, etc. Within the same group may be included the greater part of organic carburizing substances, which, at the temperature of cementation, become decomposed with liberation of carbon. These substances are often used in the art of cementation, mixed with each other or with various salts (especially carbonates and cyanides). The substances of this group constitute the principal solid agents used in the art of cementation.

(b) The salts derived from cyanogen (cyanides, ferrocyanides, etc.). Such substances—which, at the temperature of cementation, are fused—constitute the most important liquid agents used in the art.

(c) Hydrocarbon compounds either in the state of gas or vapor.

(d) Carbon monoxide.

The substances indicated in the two groups (c) and (d) constitute the principal gaseous agents used in the art. The so-called "mixed" agents result from the use of substances of group (a) together with carbon monoxide.

(10) This being understood, the conclusions indicated above may be resumed in the following propositions:

(A) The direct carburizing action (for simple solutions) of the carbon in the form in which it is commonly used in the solid agents [group (a)] is very slight. It may in fact be considered as absolutely negligible from the practical viewpoint.

(B) The salts derived from cyanogen (cyanides, ferrocyanides, etc.) taken alone, exercise on iron a specific carburizing action and quite intense in degree, which, however, has not yet been studied with precision. In any event it appears to be demonstrated with assurance that—contrary to what many experimenters have believed themselves able to affirm—the activity of the agents which contain carbonates of the alkaline metals or of the alkaline earths joined with free carbon, is not due to the formation and intervention of such salts. The activity of such substances is on the contrary due almost exclusively to the intervention of the carbon monoxide which is formed by the action of the coal on the carbonic anhydride formed by the dissociation of the carbonates.

(C) The carburizing action exercised by charcoal in the presence of an atmosphere of nitrogen alone is practically negligible.

(D) In the carburizing action exercised on iron by volatile hydrocarbons at a high temperature, there certainly intervenes in notable degree, the direct action of the gas (by diffusion). There are lacking, however, experimental data suited to determine in what degree there may intervene—joined to this action—a further direct action of the carbon finely divided, which the hydrocarbons in decomposition deposit on the surface of the iron.

(E) The carburizing activity which pure carbon monoxide exercises on iron at the temperature adopted in practice for cementation, is due exclusively to the specific direct action of the gas.

(F) The specific carburizing action of carbon monoxide becomes most intense when the gas acts on the iron in the presence of free carbon. Such specific action—modified by other carburizing substances present, such as hydrocarbon, cyanides, etc.—is markedly preponderant over all other actions in all the agents in which carbon monoxide is present or may be formed. This is the case practically in all solid agents used in the art.

It is not possible here to illustrate and to demonstrate these propositions. Such illustration and demonstration in complete and extended form may be found in the publications indicated at the end of the present paper.

(11) Re-assuming the content of the various propositions

above noted, we may affirm that the carburizing action of all the agents used in the technique of the art is due to the direct intervention of carburizing gases, which are diffused as such in the mass of the metal, to which they yield the free carbon resulting from their partial decomposition. Such carbon enters into union with the iron in the locality where it is liberated from the gas, giving rise to a solid solution of carbide of iron (Fe_3C) in the iron present in excess.

The carburizing gases which form in such manner the really active part of all the agents used in the art, may be noted in three principal groups:

(a) Cyanogen and its Volatile Derivatives. Such gases develop in the liquid agents composed of cyanides and of ferrocyanides in a state of fusion.

(b) Hydrocarbons. The action of such gases intervenes in preponderating degree—not only in the gaseous agents formed from volatile hydrocarbons—but also in the solid agents containing (commonly together with the various forms of charcoal) organic substances decomposable at the temperature of cementation.

(c) Carbon Monoxide. The direct action of this gas intervenes in manner absolutely preponderant in a great number of solid and mixed agents used in the art. It appears isolated in the mixed agent composed of granular charcoal maintained in an atmosphere of carbon monoxide.

(12) The mechanism of the direct carburizing action which the gases mentioned above exercise by way of diffusion in the steel, is similar for all the gases of the three groups; and is characterized by the reaction velocity for the reactions which give rise to the decomposition of the various gases, and by the various states of equilibrium to which the reactions lead, under the varying conditions in which they proceed.

However, for the gases of the first two groups (cyanogen and hydrocarbons) the reactions which give rise to the liberation of free carbon are very complicated; so that in practice it is not possible to determine the details with precision, and it is necessary to be content with an empirical consideration of the general characteristics and of the final results. In the case of carbon monoxide, on the other hand, these reactions are very sim-

ple and it is easy to take exact account of their progress in detail.

It seems, therefore, desirable to examine here, briefly, the latter case (which is moreover the one of highest importance in the art) and to pass the others by with the understanding that; although much more complicated, they are analogous in general character.

(13) The details of the reactions to which is due the specific carburizing action exercised by carbon monoxide on steel, at temperatures above 850° C, may be schematically explained in the following manner.

The carbon monoxide—especially when it is found in contact with iron which, acting as an energetic catalyzer, facilitates its decomposition—splits, at the temperature of cementation, into carbon and carbon dioxide in accordance with the following reversible reaction:

$$2\,CO \rightleftarrows CO_2 + C$$

When all the carbon which is liberated as the result of this reaction passes into the state of solid solution of carbide of iron in the iron, and when the operation is prolonged to the point of reaching a true state of complete chemical equilibrium, the state of such equilibrium depends on the total pressure of the gaseous atmosphere, on the partial final pressure of each one of the two gases (CO and CO_2), on the temperature of the system and on the concentration reached by the carbon in the solid solution: or (what is more directly interesting in practice) this latter concentration depends on the other variables above noted.

If we now examine the case in which the carbon monoxide acts in the presence of the solid carbon (as happens in the greater number of practical cases) the relation between the partial pressures of the two gases present (CO and CO_2) in equilibrium with the free carbon, assumes, for every temperature and for every total pressure of the gaseous atmosphere, a well determined value. And up to the point where such value corresponds to a partial pressure of the carbon monoxide superior to that corresponding on its part to the equilibrium of the gaseous mixture with the carbon in solution in the iron in the form of carbide—the reaction above written will continue to

progress in the sense from left to right, and continuously new quantities of carbon will pass into solid solution in the superficial layers of the steel. In such a case, so long as no other phenomenon intervenes, equilibrium will be reached and the reaction will stop as soon as the concentration of the carbon in such strata reaches a value such as to produce a state of chemical equilibrium with the same gaseous mixture which is in equilibrium with the free carbon.

(14) But the phenomenon can assume such a simple form, purely static, only in the case in which there does not intervene contemporaneously the process of gradual diffusion of the gases into the mass of steel subjected to cementation.

In fact when the gaseous mixture of carbon monoxide and carbon dioxide, which finds itself in equilibrium at a given temperature with the carbon dissolved (in the state of carbide of iron) in the outer carburized stratum of the steel, reaches contact, by the process of diffusion in the metal, with the steel of the deeper strata, and in which the concentration of the carbon is less, and with which therefore it will not be in equilibrium, it yields to the iron gamma a little carbon, augmenting its holding of carbon dioxide. This brings about an oxidization anew of a part of the carbon at higher concentration contained in the exterior strata, and so the operation proceeds.

In this manner, in short, the carbon monoxide—mixed with a proportion of carbon dioxide, variable according to the physical conditions of the process—diffusing itself in the mass of the steel, deposits in strata gradually deeper and deeper, ever new quantities of carbon which remain there in a state of solid solution and effect thus—by way of the phenomena above noted—an equalizing action on the concentration of the carbon and prevent such concentration from rising too high in the outer layers of the steel subjected to the process.

Thus the process of carburization of the steel proceeds in such manner that the concentration of the carbon—in an external layer of the metal, the thickness of which increases gradually with the progress of the operation—reaches the maximum value corresponding to chemical equilibrium with the carburizing gaseous atmosphere, which, in its turn, is found in equilibrium with the free carbon with which it is in contact.

The progress of such reactions and the final condition reached as a result of them, depend first of all on the physical conditions under which the operation is carried out; and it is clear that the causes which tend to turn toward the right the conditions of equilibrium of the reversible system

$$2\,CO \rightleftarrows CO_2 + C$$

must necessarily give rise to an augmentation in the concentration of the carbon which passes into solid solution in the gamma iron of the treated zone. And it is to be noted that among such causes must be counted especially, lowering of the temperature and increase of pressure; because we are here concerned with an exothermic reaction which is accompanied by a diminution of volume. In cases where the carbon monoxide acts in a mixture with other gases practically inert (for example nitrogen) its pressure is the component of the total pressure due to the gaseous mixture, and this is, moreover, proportional to the concentration of the carbon monoxide in the mixture.

The final state reached by the system, depends then, in the largest measure—for the reasons which I have noted in the early part of this same section—on the relative reaction velocities of the various chemical reactions which are here involved, and on the velocity of the different phenomena of solution of the carbon and of diffusion of the gases in the metal. The effects of these concomitant causes often reach, in practice, such intensity as to mask and even to invert those of the principal causes first noted.

(15) It is not possible to develop here—from evident limitations of space—a complete and detailed examination of the phenomena noted; and still less to discuss the relations of cause and effect which operate between the conditions under which the phenomena proceed and the characteristics, both qualitative and quantitative, of the products obtained. For such matters of detail I must limit myself to refer those interested to the accompanying bibliography.

From what has been above noted in an elementary manner, it clearly results nevertheless that, having in view the extreme simplicity of the reaction to which is due the carburizing action of carbon monoxide on iron, and likewise the fact that such prin-

cipal reaction is not accompanied by any of the numerous "parasitic" reactions which always accompany the action of all other agents, in some cases by their intensity and practical importance assuming a dominant position over the fundamental reaction, the effects of which are thus masked and profoundly modified—having these facts in view, it appears that the process of carburization due to the specific action of carbon monoxide may be considered as the typical process for the cementation or case-hardening of steel.

It is further also evident that the same simplicity of the laws which regulate the details of the process of cementation in which carbon monoxide operates as the only—or at least as the absolutely preponderating—carburizing agent, should characterize those by means of which definite results and products best responding to the purposes for which they are intended, may at will be obtained with ease and assurance.

CHAPTER II.

CHARACTERISTICS OF THE VARIOUS CARBURIZING SUBSTANCES AND THEIR USE.

(16) The principal conditions, which, in the greater number of practical cases, it is necessary to realize in the most complete, precise and certain manner in order that, by means of successive heat treatments to which it must be subjected, it may be possible to impart to the piece subjected to case hardening, the properties which will render it suited to meet the requirements for which it is intended, are the following:

(a) The maximum velocity of cementation: understanding by "velocity", the depth reached in a given time by the carburized stratum. Such condition has not only an economic importance (evident by itself) but is also technically important because the qualities of many steels may become seriously affected by too prolonged a heating at the elevated temperature of the process.

From this view point the agents in which the carburizing action is due only, or at least in predominant part, to carbon monoxide, are clearly superior to all others.

(b) Definite assurance of obtaining a carburized zone of the desired depth.

(c) Definite assurance of reaching, in a determinate portion of the carburized zone, a concentration of the carbon predetermined as the minimum value requisite in order to impart to the steel of this part of the piece (by means of heat treatments) the desired hardness.

(d) Definite assurance that the concentration of the carbon shall not exceed in any point in the carburized zone (and in particular in the outer layers) a maximum value, predetermined with a view of avoiding excessive brittleness in the metal.

The brittleness of the carburized zone, in the outer layers of which the concentration of the carbon has reached a value too high, is due principally to the formation—in such strata—of numerous laminae of cementite: such laminae are fragile and give rise readily to surfaces of fracture.

The two figures 1 and 2, reproduce in fact, with a magnification of 50 diameters, the micro-structure of the outer region (upper part of the two figures) of two pieces of steel, case-hardened under different conditions. In the first, the concentration of the carbon of the outer strata exceeded 1.3%. Note especially (see the upper part of the figure) the characteristic fragile veins of cementite, which on the other hand are lacking in the other specimen, in which the concentration of the carbon, even in the superficial layer (formed of pure pearlite) does not exceed 0.9%.

In order to better fix the ideas regarding the concentrations of the carbon which are characteristic of the two types of carburized zone (fragile and non-fragile) attention is called to the two following figures (3 and 4) showing two diagrams of the distribution of the carbon in the same two zones shown by the preceding photo-micrographs. In the two diagrams the abscissae correspond to the depth of the various strata analyzed, starting from the outer surface, while the ordinates represent the concentration of the carbon, determined by means of chemical analyses from these individual strata. The diagram of Fig. 3 corresponds to the photo-micrograph Fig. 1 and that of Fig. 4 to the photo-micrograph of Fig. 2.

(e) Definite assurance of obtaining, in the carburized zone, the most suitable distribution of the concentration of the carbon; and this, especially in the sense that such concentration shall

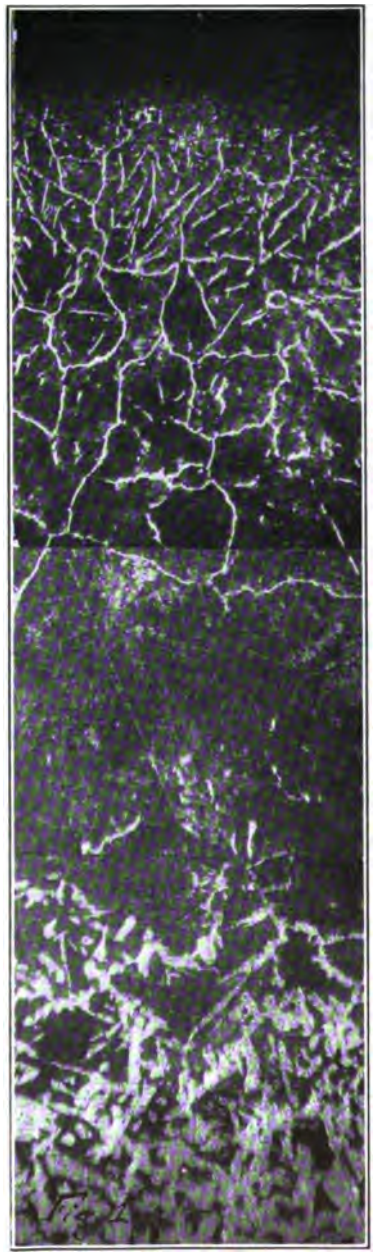

Fig. 1 (x50). Micro-structure of the Outer Region of a Piece of Case-hardened Steel. Concentration of Carbon in Outer Strata Exceeds 1.3 Percent.

diminish in a gradual and continuous manner from the outer layers of the piece to those lying deeper and deeper, without presenting abrupt change, and in correspondence with which are

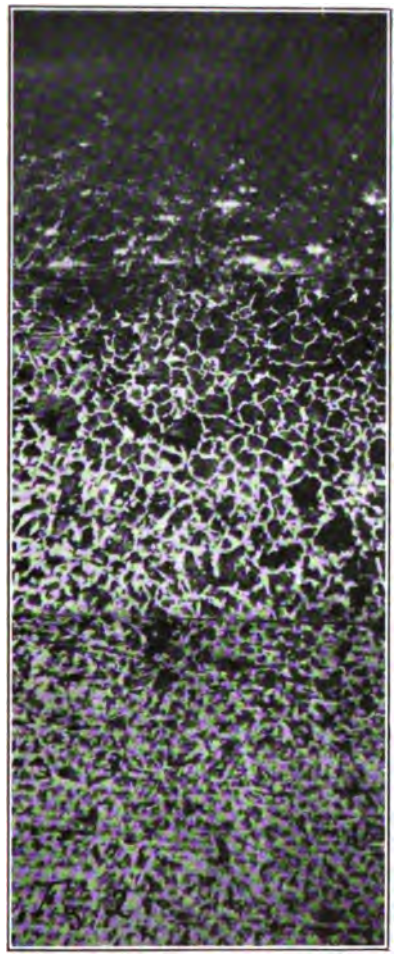

Fig. 2 (x50). Micro-structure of the Outer Region of a Piece of Case-Hardened Steel. Concentration of Carbon does not Exceed 0.9 Percent.

always found (after quenching) phenomena of brittleness which manifest themselves especially under the form of exfoliating cracks in the piece subjected to the process.

The principal cause of abrupt discontinuities in the variation of the concentration of the carbon in the successive strata of the carburized zone is dependent on the phenomenon of segregation of the cementite and of the ferrite which occurs during the cooling of the piece, especially if in the treated zone the concentration of the carbon reaches especially high values.

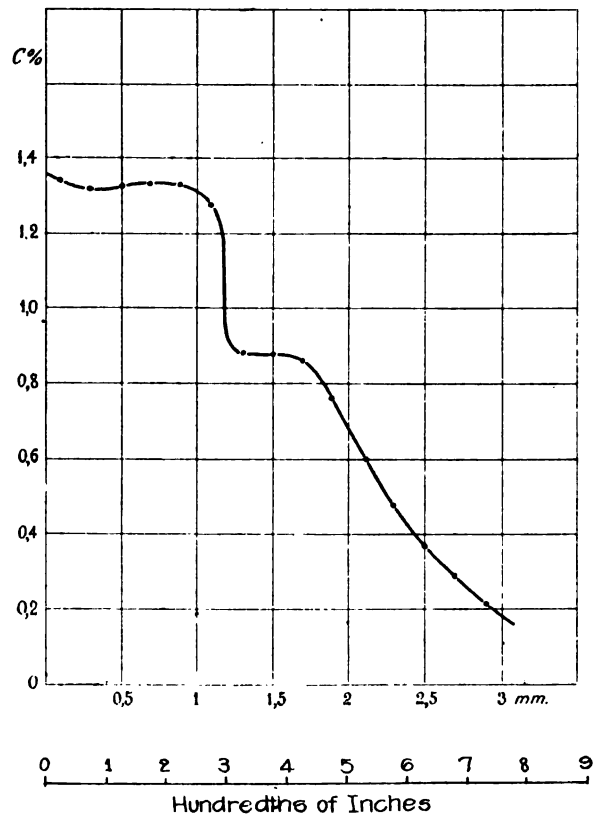

Fig. 3. Diagram Corresponding to Fig. 1.

Such phenomena—to which I can here give only the briefest reference—have as their result a marked accumulation of carbon in certain determinate strata of the carburized zone, so that, between these strata and those lying immediately adjacent, there exists an abrupt change in the concentration of the carbon.

This fact appears clearly from an examination of the diagram of Fig. 3 which represents (in the manner above described) the distribution of the carbon in a carburized zone in which are to be noted the phenomena of segregation referred to above. Thus, in this diagram, it is clearly seen

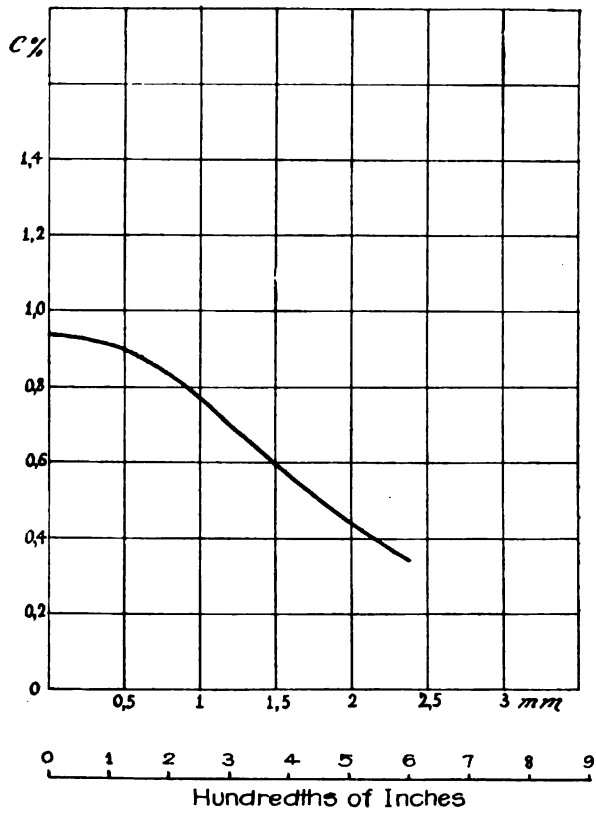

Fig. 4. Diagram Corresponding to Fig. 2.

that the concentration of the carbon falls abruptly from 1.3% to 0.9% in passing from the stratum at 1.2 mm (0.048 inch) depth to that adjacent at a depth of 1.3 mm (0.052 inch).

(17) For the reasons which I have already noted, the conditions indicated in the preceding paragraph may be realized in the best and most certain manner by adopting agents, the activity of which is due exclusively or in absolutely preponderant

degree, to the specific action of carbon monoxide. Such agents, employed under conditions of temperature and of pressure, definitely determined—fundamentally by reference to the theoretical concepts to which I have made reference above—permit the realization in practice of all the conditions indicated in the preceding paragraph.

These are known in the art and by reason of this fact under the name of "gradual" agents to distinguish them from the others (especially nitrogenous organic substances, hydrocarbons, cyanides and ferrocyanides) which are called "abrupt" agents, because they furnish cementation characterized by a sudden and marked elevation in the concentration of the carbon, and which with difficulty admits of regulation with variation in the conditions of operation, and gives rise to carburized zones, which—for reasons above noted—present, in determinate regions of their thickness, abrupt variations in the concentration of the carbon.

(18) The most important group of "gradual" agents used in the art is the following:

(a) Agents constituted of different forms of charcoal—powdered or granular—formed in preponderant degree of pure carbon and arising from the decomposition of organic substances.

Such are the charcoals derived from various types of wood, calcined lampblack and bone charcoal, also calcined.

The activity of these agents is due almost exclusively to the action of the carbon monoxide which is formed by the reaction of the coal on the oxygen of the air which impregnates its mass.

For charcoals deprived of organic residues and of salts (especially carbonates) the carbon monoxide is very much diluted by the nitrogen of the air from which it is derived. They are thus agents very "gradual", suited to give case-hardened zones with low or moderate carbon content. Such agents exhaust themselves quickly by the gradual dispersion, by diffusion, of the small amount of carbon monoxide which they contain.

In proportion as the percentage of undecomposed organic residue contained in the coal is increased, their "abrupt" carburizing action—similar to that of the hydrocarbons which we shall examine later—is added to the "gradual" action of the carbon monoxide, and agents are obtained less and less "gradual" in operation. Such are animal charcoal only slightly

burned, and soot obtained at low temperature. Agents endowed with analogous properties are obtained by mixing with charcoal varying proportions of organic substances (sawdust, oils, etc.).

(b) The agents formed by mixtures of powdered or granular charcoal with carbonates which undergo dissociation at high temperature.

The activity of such agents is due almost exclusively to the action of the carbon monoxide which is formed by the reaction of the charcoal on the carbonic anhydride arising from the dissociation of the carbonates. The active carburizing atmosphere which impregnates these agents, being formed in absolutely preponderant degree of pure carbon monoxide (which, developing as a result of heat, drives out of the receptacle in which the process is carried on, the greater part of the nitrogen of the air which was contained there) its action is more intense and more rapid than that of the cements in (a). But when this operation is not carried out at too high temperatures these agents may still be considered as "gradual".

The quantity of carbonic anhydride which develops from the carbonates contained in agents of this group being limited, they become exhausted in very long operations by the diffusion of the gas beyond the receptacle in which the operation is carried out. However, the agents themselves may be, at least in part, regenerated by exposure to the air after having been used. In such case, in fact, the products of the dissociation of the carbonates contained in them, absorb from the atmosphere a part, larger or smaller, of the carbonic anhydride which they had lost by heating.

The agent of this group most commonly used is that formed of 60 parts of powdered wood charcoal mixed with 40 parts of carbonate of barium, also pulverized. This is known under the name of "Caron's cement" because it was proposed by Caron some fifty years ago. This is the most easily regulated, the most effective and the most readily regenerated of all the agents of its class.

Other agents of the same class are those formed of powdered charcoal mixed with variable proportions (from 2 to 15 percent) of alkaline carbonates and alkaline earths.

(c) The agent composed of simple wood charcoal in a granu-

lar condition through which is caused to circulate a more or less slow current of carbon monoxide. In practice, with the velocity of the reactions which are involved in these conditions, the carbon monoxide may be replaced with carbonic anhydride.

After what I have already said—especially in sections (13), (14) and (15)—it is easily understood that this agent operates in practice exclusively by the specific action exercised by carbon monoxide on the iron, the charcoal serving simply to regenerate, in continuous manner, the mixture of carbonizing gases, thus maintaining in them a constant proportion between the concentrations of the two constituents (CO and CO_2).

This is the agent in which may best be regulated the action of the carburizing substance. Furthermore, in this agent is utilized in the best manner the characteristic rapidity of cementation by carbon monoxide. This is, in fact, practically inexhaustible, because it is easy to bring into the receptacle in which the operation is carried on, a gentle current of carbon monoxide (or of carbonic anhydride) thus compensating for the small loss of the carburizing gas due to the operation of diffusion.

The action of this agent may be rendered more rapid in determinate measure by augmenting the temperature or the pressure, or by mixing with the gas which circulates in the case-hardening receptacle a determinate quantity of gaseous hydrocarbon. It may, on the other hand, be rendered more "gradual" by diminishing the partial pressure of the carburizing gas, and this may be realized by simply adding a determinate quantity of air to the carbonic anhydride which is circulated through the case-hardening chamber.

(d) The agent composed simply of pure carbon monoxide. For reasons which it does not seem necessary to present here, and also because being purely negative they have no direct practical interest, this cement is too mild. It is scarcely ever used in practice, because in the conditions in which it might be applied in the art of case-hardening, it would furnish carburized zones with too low a percentage of carbon.

(19) As I have already noted [section (17)] in contradistinction to the "gradual" agents above enumerated, attention must be given to the "abrupt" agents, characterized by the

fact that they give rise to carburized zones in which the concentration of the carbon rises most rapidly to very high values, especially in the external layers; so that in the passage from these layers to those next below, the concentration itself undergoes an abrupt decrease. These facts—which are the cause of dangerous phenomena of brittleness in the treated and hardened zone—are most strongly accentuated when the operation is carried out at a somewhat elevated temperature (for example above 850° C) or if the duration of the operation is somewhat prolonged so as to obtain a carburized zone superior to 1 mm or 1.5 mm (0.04 to 0.06 inch) in thickness. For these reasons agents of this class are not practical unless perhaps in cases in which it is sufficient to obtain a carburized zone of very little thickness (a few tenths of a millimeter), or in which the treated piece will not be called on to withstand violent shocks. Such cases are found, for example, with pinions or gears intended to operate in continuous manner and under a small load, for stems of valves, etc. The agents of this class ("abrupt") may be noted under the following principal groups:

(e) Organic substances, pulverized. Nitrogenous substances in particular are employed, as for example filings or scrapings of horns, hoofs or hides of various animals, leather parings, etc. There are also often used residues from oily grains, sawdust, etc.

(f) Gaseous hydrocarbons (illuminating gas, acetylene) or certain liquids in the state of vapor (benzol, petrol, etc.).

(g) Cyanides, ferrocyanides or ferricyanides in the state of fusion.

Beyond the objections noted above, these agents present those—still more serious in practice—derived from the great complexity of the reactions to which their carburizing action is due. In consequence it becomes most difficult to regulate the action in such manner as to obtain with certainty the desired results.

Such reasons exclude the use of these agents in the greater number of practical cases, and in special degree in those cases in which it is desired to obtain (as for example in armor plates) a very deep zone of cemented steel and endowed with determinate mechanical properties.

CHAPTER III.

TECHNICAL CONDITIONS FOR THE USE OF THE VARIOUS TYPES OF CARBURIZING MATERIAL.

(20) In what concerns the mode of using, in practice, the various carburizing materials which I have above classified in accordance with their characteristic mode of operation, they may be subdivided into four groups.

(1) Solid agents (comprising those which I have noted under the letters (a, b, e). (2) Liquid agents, g. (3), Gaseous agents, d, f. (4), Mixed agents, c.

The various agents appertaining to each of these groups are used under approximately the same conditions. Let us see, briefly, what the conditions are for each of the groups. These vary naturally with variation in the dimensions and in the form of the piece which it is desired to subject to the process.

(21) For the treatment of pieces of medium and small dimensions, and the weight of which may vary from a few grams to a maximum of 300 to 400 kilos (660 to 880 pounds) (usually members of machines or tools), the case hardening with solid agents is carried out in a closed box or pot. On the bottom of a box of cast or sheet steel of appropriate dimensions, a layer of the carburizing substance is placed of some few centimeters thickness (1 inch or more) on which is placed a first layer of the pieces to be subjected to the process and so spaced that between them there is a distance of at least three or four centimeters (1.20 to 1.60 inch). On this first layer of pieces is then placed a layer of carburizing material which covers it entirely, taking care to see that it fills in completely the spaces between the parts. On this new layer of material may be placed a second series of pieces, then more material and so on until the box is filled. The box is then closed with a cover of sheet steel, care being taken to lute well the joint with some refractory material. In Fig. 5 is shown a box thus charged. The boxes are then introduced into a reverberatory furnace and slowly heated to the temperature required (usually between 850° and 1050° C.). The furnace used for this purpose does not present anything unusual in its construction. Use is made of furnaces heated either

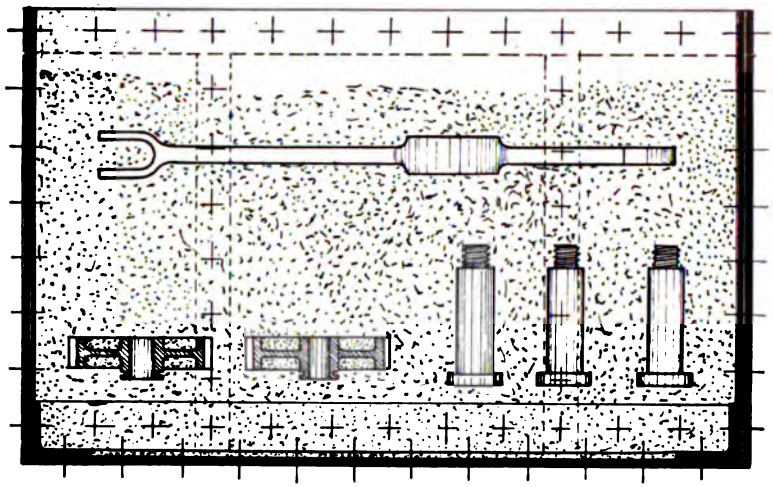

Fig. 5. Box for Case-hardening Small Pieces of Steel with Solid Agents.

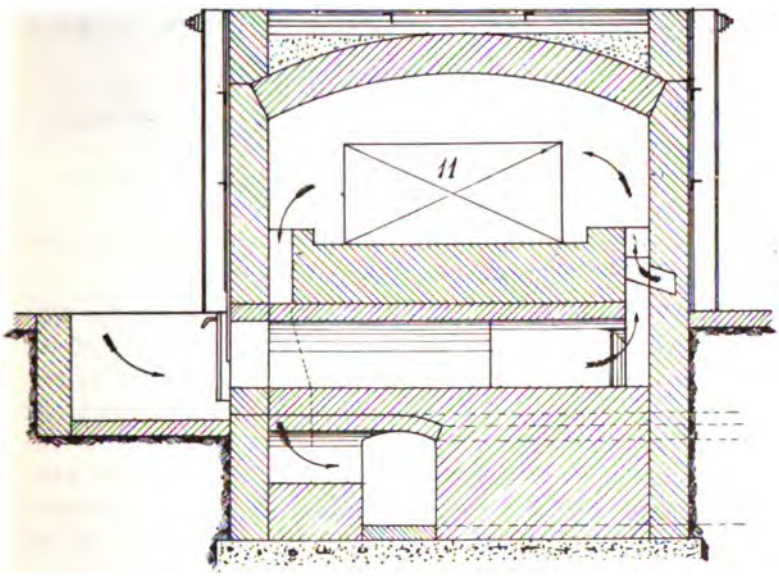

Fig. 6. Furnace in which are Heated Boxes of the Type shown in Fig. 5.

directly by coal or by producer gas, or by heavy oils or even by illuminating gas. Fig. 6 represents the transverse section of such a furnace heated by producer gas. In the furnace is placed a box (11). The following figure (Fig. 7) shows in perspective a group of case-hardening furnaces of the type shown in Fig. 6.

The operation being completed, the boxes are removed from the furnace and—after slow cooling—are opened in order to take out the case-hardened pieces, which are then subjected to heat treatment in the manner noted later on.

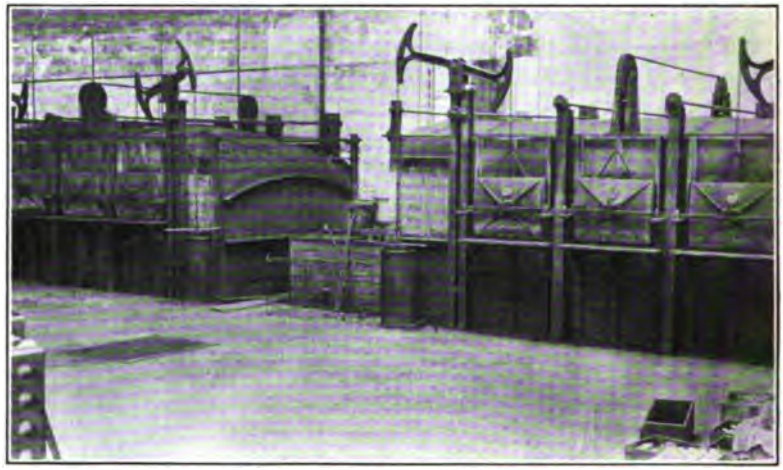

Fig. 7. Group of Case-hardening Furnaces of Type shown in Fig. 6.

The most serious objections in practice to the use of the pot or box in this manner, are the following:

(1) The long time which is necessary in order for the temperature of cementation (reached rapidly in the strata of the mass adjacent to the walls of the pot) to penetrate to the central regions. The consequences of this fact are: The long duration, and hence the high cost, of the operation; irregularity in the degree of carburization which results highest in the parts adjacent to the walls of the pot and minimum in the parts located toward the center; and finally, the serious deformation of the pieces subjected to the process, due to the varying degree of heating in different parts of the same piece.

(2) The large consumption of pots, the cost of which increases seriously the cost of the process.

(3) The difficulty of controlling the actual temperature of the pieces subjected to the process, it being necessary in practice to be content with the determination of the temperature of the outside of the receptacle.

An effort has been made to obviate in part the last named objection by making holes in the cover of the receptacle, through which are introduced rods of steel, allowing an end to project outside, and extending on the inside to the center of the mass contained therein. Withdrawing one of these rods (called spies) from time to time, quenching it and examining the fracture, will then furnish the basis for a judgment as to the progress of the operation. Such a procedure is, however, not without certain practical difficulties.

When it is desired to make use of solid materials for very deep cementation, as for example in the complete cementation of the bars of iron which are to be transformed into cast steel (see section 6), use is made of a receptacle or case formed of refractory material inclosed in a cementation furnace. In such case the objections noted above as inherent in the use of the pot or box appear in still stronger degree, with the exception of No. 2.

Solid materials are also used for the case-hardening of armor plates, in which case the two plates are disposed horizontally in a furnace with the two surfaces to be treated placed face to face in such manner that these form by themselves two of the walls of the cementation box. In the interval between the two plates is placed the material, and the closure of the box is completed with walls of refractory material, luted tight. Under these conditions a complete operation requires from 18 to 45 days according to the thickness of the plate.

(22) The liquid substances—used in practice (for the reasons already noted), for the treatment of pieces of small dimension only, (calipers, pivots, various cutting tools, etc.), are employed in two essentially different ways.

(A) Immersing the piece to be treated in the fused carburizing material (usually cyanide of potassium).

(B) Sprinkling the piece to be treated, after having heated it red hot, with pulverized material (usually ferrocyanide of

potassium) and continuing the heating—for example over a forge fire—in such manner as to melt the material which then forms a species of "varnish" over the piece.

The second procedure is used only when it is desired to obtain carburized zones of a thickness not exceeding two or three tenths of a millimeter (0.008 to 0.012 inch).

(23) The use of gaseous carburizing agents for the case-hardening of mechanical parts of small or of medium dimension is not widely diffused and this for the reason already noted (See section 18 d, and 19). However there are made and on sale special rotative furnaces, very ingenious and intended to render practicable the use of this form of agent.

Gaseous agents (illuminating gas) are, on the other hand, still used for the case-hardening of armor plates. In such case two plates are disposed horizontally in a furnace, in such manner as to form—with the aid of steel bars disposed between them about the edge—a genuine cementation box, in the interior of which the illuminating gas is caused to flow.

This process—introduced into the art by the Schneider Co. —has the objection of giving rise to an excessive concentration of carbon in the external part of the plate. Such part is then liable to become brittle as a result of the heat treatment, which may produce also deep cracks similar to those shown in the armor plate reproduced in Fig. 8. The width of the cracks in the plate here shown, exceeds in several places a half centimeter (.2 inch). For these reasons, and also for others on which I can not here pause—this process is no longer used or only by a few makers of armor plate who may prefer to avoid the difficulties of treatment with solid agents (see preceding section) and consisting chiefly in the much greater cost due to the longer duration of the operation.

(24) Among the mixed agents properly so called, the only one used in the art is that composed of a granular mass of charcoal, through which is caused to circulate a current of carbonic anhydride, pure or mixed with other gases, suited to regulate the action.

Of the mode of operation of this agent—the only one which permits the utilization in a complete manner of the advantages presented by the specific carburizing action of carbon monoxide

—I have already spoken. Let us see here, briefly, how it is used in practice in the chief typical cases.

(A) For the case-hardening of mechanical parts of small or medium dimension, there is used, preferably, a vertical muffle furnace, of the type of that reproduced in vertical section in

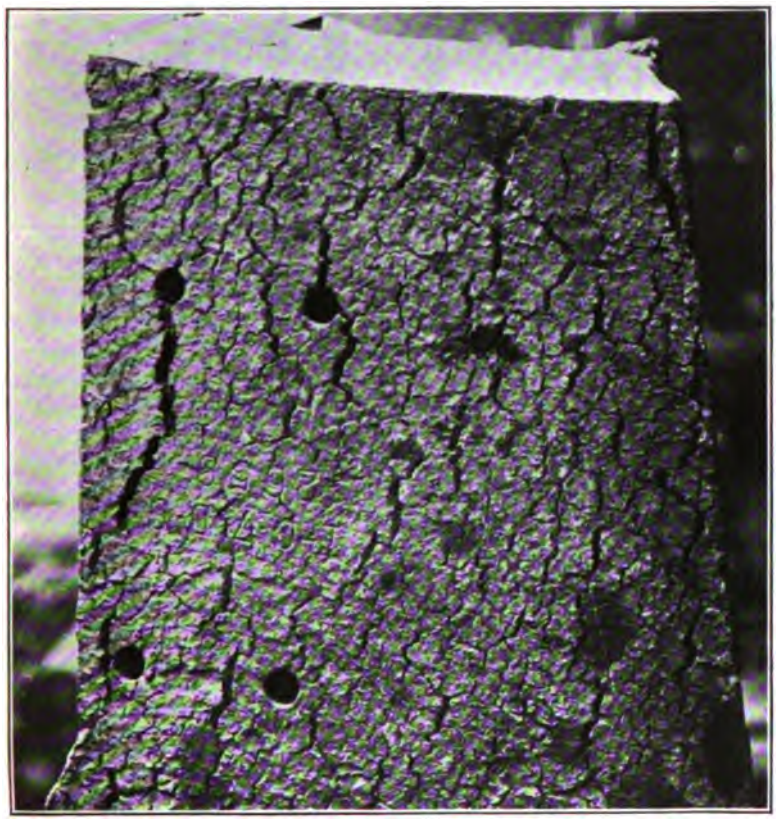

Fig. 8. Armor Plate Case-hardened with Gaseous Agents. Excessive Concentration of Carbon at Face Causes Cracks to Develop.

Fig. 9. In this furnace, heated by gas producer fuel, the pieces are charged into the furnace from the top A, (see Figs. 10, 11 and 12), and are carried by the movable bottom F, Fig. 9. On this is placed the granulated charcoal and the current of carbonic anhydride is brought in through the tube D. The opera-

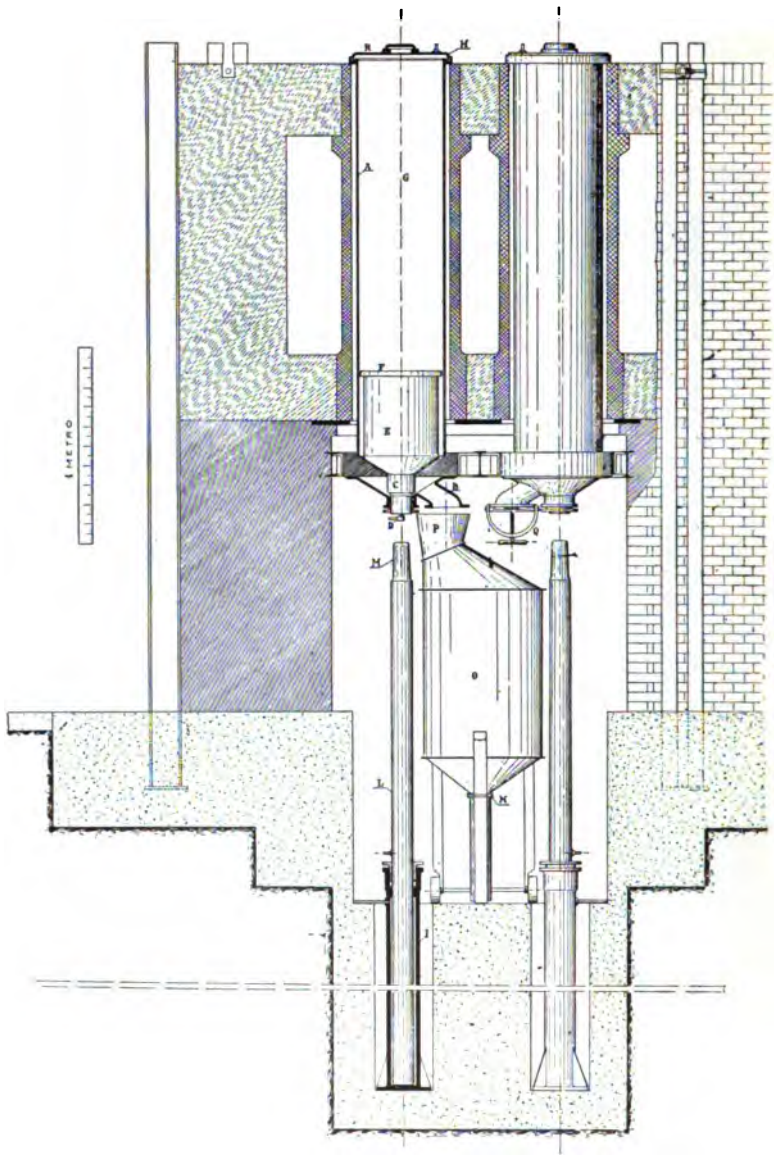

Fig. 9. Vertical Muffle Furnace for Case-hardening Mechanical Parts of Small or Medium Dimensions.

tion being completed, the granular charcoal is removed by way of the channel B into the receptacle O, from which it is quickly turned into another muffle already charged with pieces, in such manner as to use it while still hot. The treated pieces are withdrawn with the greatest facility by raising them to the level of the upper mouth of the furnace by means of the movable bottom F, which is pushed up by a hydraulic lift.

Furnaces of this type are also constructed, heated by illuminating gas or by mineral oil (see Fig. 13).

The process here noted, while it permits of the complete utilization of the most advantageous properties of carbon monoxide—of which I have already spoken—eliminates in practice all the objections arising from the use of the case-hardening pot or box.

(B) For the complete cementation of bars of iron, the mixed agent with a base of carbon monoxide may be used in furnaces with refractory casing, similar to those which I have referred to above (see section 21) used for solid agents. The carbonic anhydride is then brought into the casing at the bottom. In this manner the complete cementation of the bars is obtained in a time not exceeding one fourth of that necessary when use is made of the ordinary solid agents.

(C) For the case-hardening of armor plates, the plates are arranged in pairs in such manner as to form the sides of a cementation box, in similar manner to the arrangement referred to for the use of gaseous agents (see section 23). However in this case, the box is preferably disposed in the furnace in such manner as to bring the plates into the vertical position.

The characteristic advantages of a mixed agent with base of carbon monoxide reach, in this case, their maximum value, permitting the reduction of the time required for the treatment of armor plates to six or seven days, and the practical elimination of brittleness in the face of the plate and of the formation of the deep cracks which characterize plates treated with "abrupt" agents.

The use of mixed agents with base of carbon monoxide, and the various methods of practical application are protected in all industrial countries by patents belonging to the Societa Anonima Italiana Gio. Ansaldo & C of Genoa.

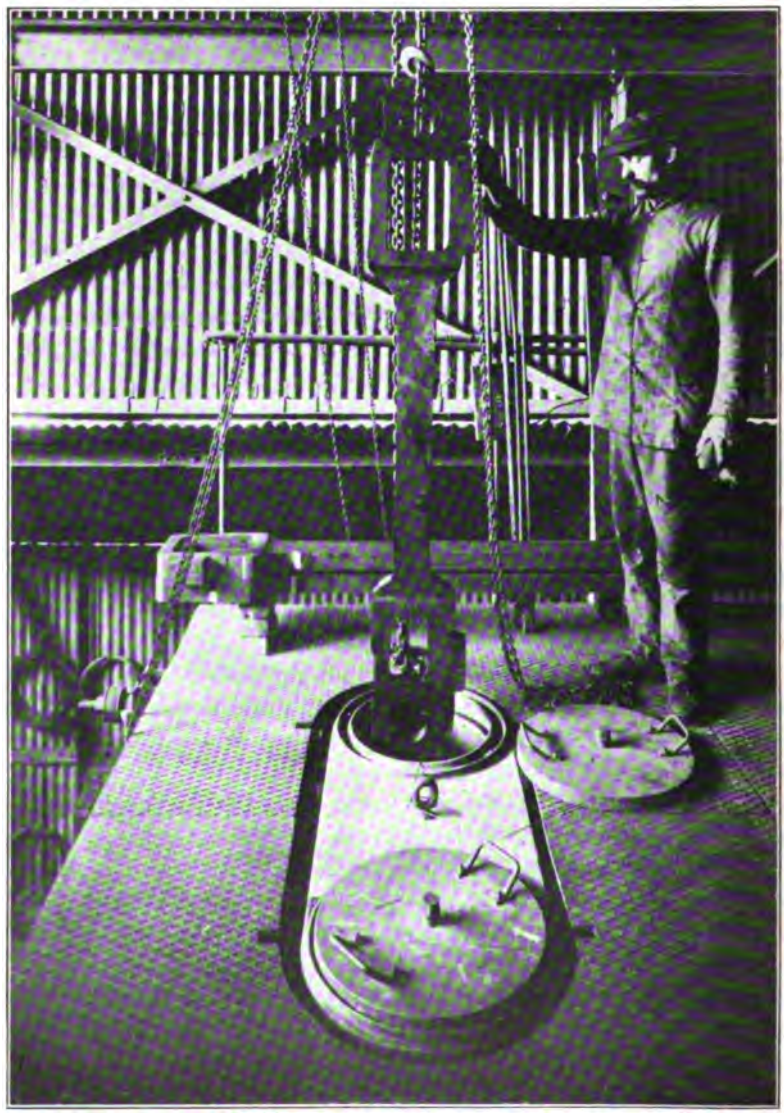

Fig. 10. Charging Furnace of Type shown in Fig. 9.

Fig. 11. Charging Furnace of Type shown in Fig. 9.

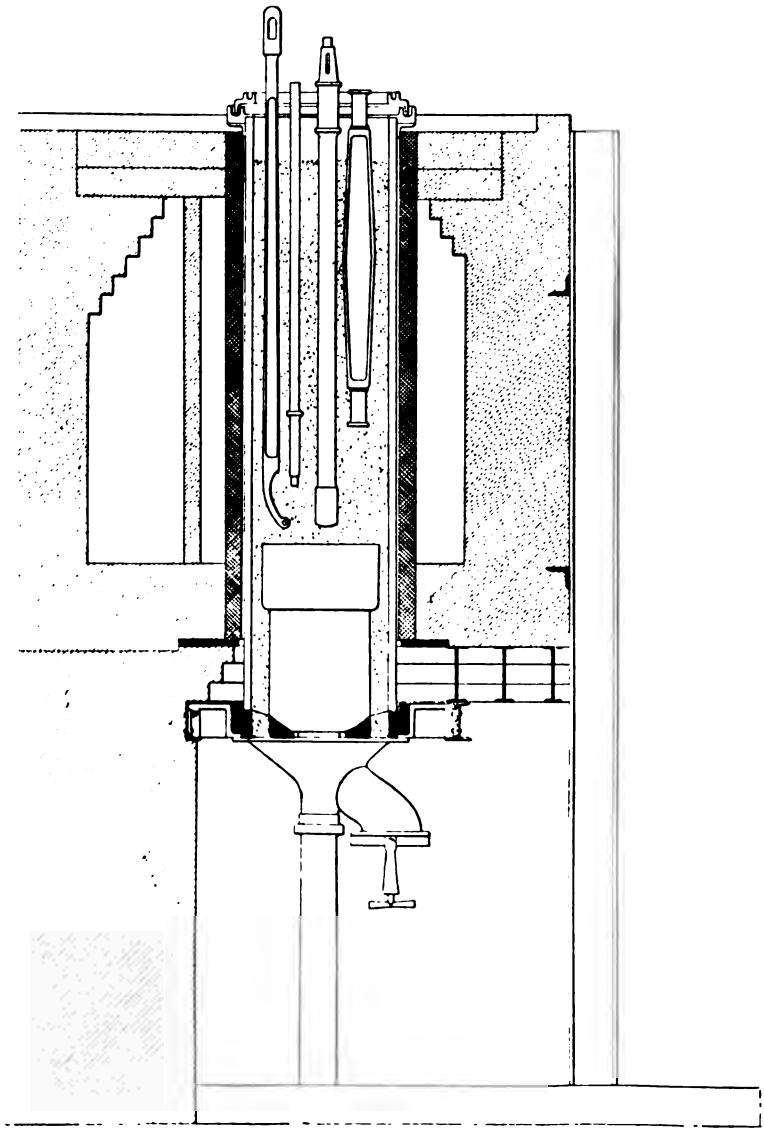

Fig. 12. Furnace of Type shown in Fig. 9 charged with Pieces to be Case-hardened.

Fig. 13. Furnace of Type shown in Fig. 9, Heated by Illuminating Gas or Mineral Oil.

CHAPTER IV.

TREATMENT AND CHARACTERISTIC PROPERTIES OF CEMENTED PARTS.

(25) Having thus examined briefly the various types of carburized zones—both as to their chemical characteristics depending on the concentration and distribution of the carbon and the various modes of carrying out the operation in practice —it is desirable to note further the technical characteristics of the pieces treated in accordance with the various methods. And since such characteristics depend in very large measure on the heat treatment to which the pieces are subjected after case-hardening, it is necessary to premise briefly with regard to such treatment.

The heat treatment of a case-hardened piece should be devised in such manner as to realize, at the same time and with the same means, two distinct purposes. The first of these is to impart the maximum strength to the metal constituting the interior of the piece ("heart") and to which the carburizing action of the agent has not reached, taking due account of the fact that such metal during the process has been overheated to a considerable degree and during a considerable time, and is, therefore, in need of some form of regenerating treatment.

The second purpose is to impart the maximum surface hardness to the treated metal in the outer layers of the piece.

Both of these purposes may be realized by "quenching" operations. The temperatures at which such quenching operations should be carried out vary notably with change in the position of the critical points of the metal constituting the various parts of the piece treated, and hence with variation in the initial composition of the steel subjected to the process. It thus appears desirable to examine briefly the problem in relation to the composition of the types of steel used most commonly for case-hardening purposes.

(A) Ordinary Carbon Steel. This is used for reasons of economy in cases where it is not necessary to obtain exceptionally high values of the strength in the body of the piece treated. Low carbon steel is preferred (usually about .10%), with manganese about .40%. In order that the preliminary quenching

(that intended to give the desired toughness to the body of the piece) may be effective, it should be carried out—for reasons well known—at a rather high temperature (in general about 900° C.) and therefore preferably in oil. It follows that such a quenching cannot impart the maximum hardness to the treated zone, so that, where necessary to obtain such maximum hardness, it is necessary to follow this first quenching with a second (usually in water) carried out at a lower temperature (usually from 750° to 780° C.). The treatment may be simplified, limiting it to the first quenching carried out at a temperature of 850° to 900° C. in cases where it is not necessary to obtain the maximum hardness in the treated zone, or to the second quenching (carried out at a temperature toward 800°) in cases where it is not necessary to obtain a great toughness of body in the treated piece.

(B) Nickel Steel. Choice is usually made of steels containing about 2% of nickel and about .10 to .20% of carbon with about .40% of manganese. With these steels it is possible to lower notably the temperature of the preliminary quenching (down towards 820° to 850°) thus realizing for the soft metal of the body of the piece a toughness superior to that which can be realized with carbon steels. These steels also permit, as well as the preceding, of obtaining good results by means of a single quenching.

With all other conditions equal, nickel steels are case-hardened a little less rapidly than carbon steels, and give carburized zones having—after quenching—a surface hardness a little inferior.

(C) Chrome Nickel Steels. Choice is usually made of steels containing from 3 to 5% of nickel, less than 1% of chromium, less than .15% of carbon and .40 to .50% of manganese. These steels are case-hardened more readily than those mentioned previously, and are very well adapted to give, by means of the double quenching (about 850° to 730° C.) higher values of the strength of body of the treated piece, with hardness in the carburized zone. They give also, by means of a single quenching (toward 800°) strength and hardness respectively superior to those obtainable with the other steels mentioned.

(26) A piece of steel, case-hardened and then subjected to

a suitable heat treatment, issues as though constituted of two parts.

(a) The central part, the strength of which should be as high as possible.

The mechanical properties of this part of the piece vary, naturally, between the widest limits, with variation in the composition of the steel employed and the treatment to which it is subjected. It may be laid down, however, that the metal which constitutes this part should present a tensile strength from 60 to

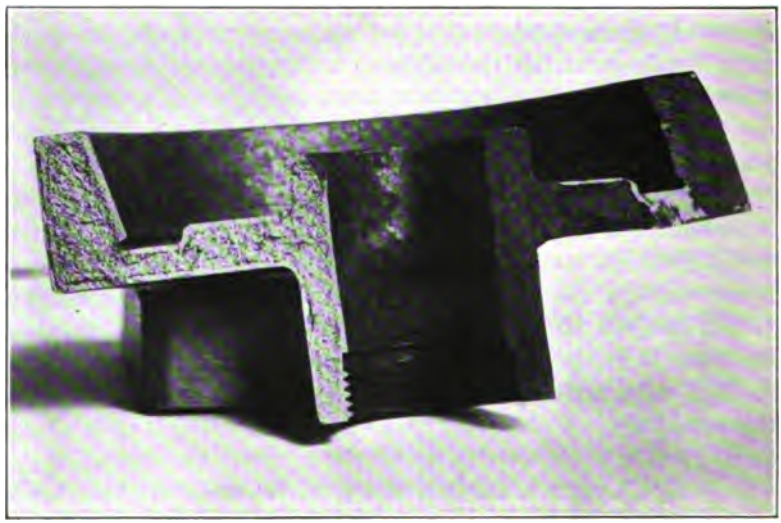

Fig. 14. Test Specimen of Chrome-Nickel-Steel which Has Been Case-Hardened. Interior Portion Presents Fibrous Structure.

90 kg. per m m² (85,000 to 128,000 pounds per square inch): an elongation exceeding 10% and a resistance to shock exceeding 7 to 10 kilogram meters per cm² (326 to 466 foot-pounds per square inch).

Ordinarily the strength of the inner part of the piece is controlled by means of a series of pieces case-hardened and treated, and broken under a hammer or by testing machine. If the strength is sufficient, the fracture of the inner part of the piece should present a fibrous characteristic. Such is the case, for example, in the test specimen shown in Fig. 14.

(b) The surface or outer layers (carburized zone) the hard-

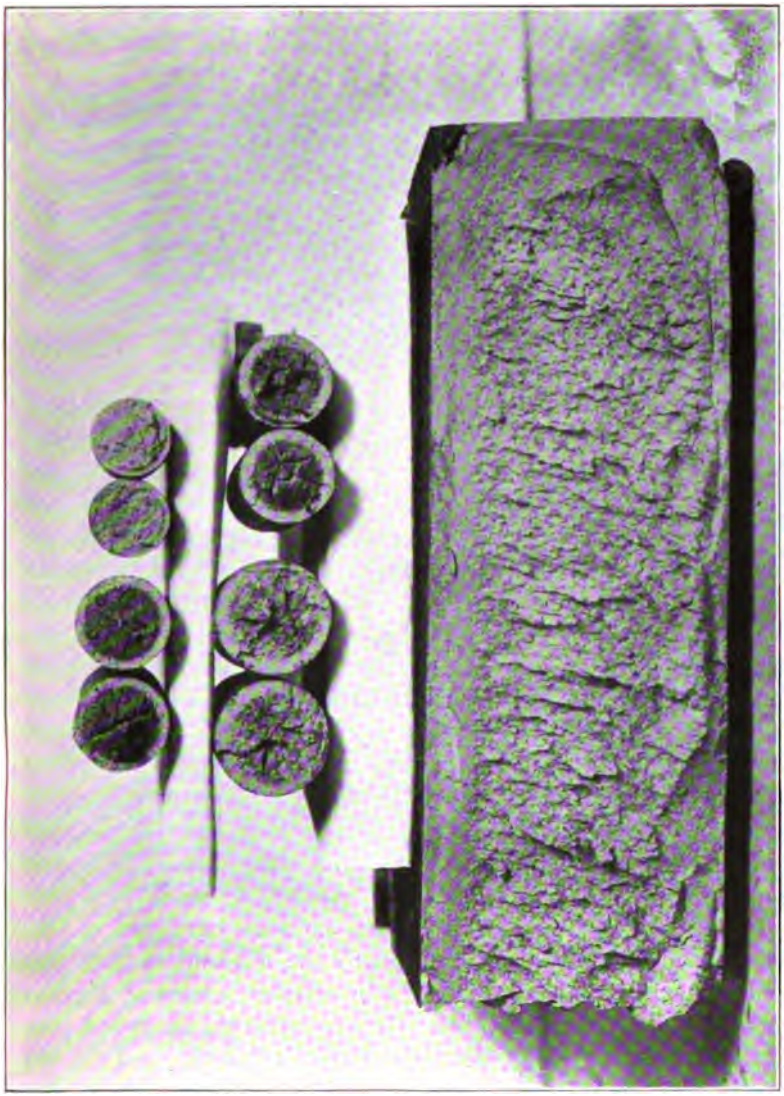

Fig. 15. Test Specimens of Chrome-Nickel-Steel showing Characteristics of Carburised Zone.

ness of which, in normal cases, should exceed that corresponding to the Brinell numbers 600 to 700.

The fracture of the metal of such a zone, obtained by breaking in testing machine or under hammer a piece case-hardened and heat-treated should show a structure with very fine grains, or even amorphous with a vitreous aspect and conchoïdal fracture. Fig. 15 shows a number of fractures with such characteristics in the case of various pieces carburized to varying depths.

I have already indicated (see section 16) the principal causes which may give rise to phenomena of brittleness in the carburized zone. Among such causes, the principal are the excessive concentration of carbon in the surface strata of the piece and the abrupt variation in such concentration between strata contiguous to the treated zone.

Having already noted the causes and the character of these facts, it appears opportune to note here briefly, with two simple examples, the characteristic manner in which their practical consequences are manifested.

(27) As to the effects of brittleness resulting from an excessive concentration of carbon due to the use of a too "abrupt" agent, they are manifest so much the more clearly the thicker the treated zone. I will cite, therefore, an example in which this last condition was present in marked degree—that of an armor plate of a thickness of 300 mm (11.8 inches). Fig. 16 reproduces the appearance of such a plate struck by a capped armor piercing projectile. The treated zone—obtained with a mixed agent with carbon monoxide as base and in which the concentration of the carbon at no point exceeded the value desired and which was subjected to a rational heat treatment—did not present the slightest brittleness.

And notwithstanding this, the extreme hardness of the treated zone is proved (other than by the mechanical tests carried out) also from the effect of another shot, aimed at a point about 90 cm (35.4 inches) from the first, with an uncapped projectile at a velocity corresponding to that ordinarily used for the acceptance test of such plates. In this second experiment, the treated zone presented a hardness sufficient to break up the projectile into small fragments and without on the other hand splintering itself in the least degree. (See shot No. 1, Fig. 16).

When, on the other hand, the concentration of the carbon reaches a value too high, the treated face of the plate becomes brittle and, under the shock of the projectile, will splinter more or less extensively, diminishing in serious degree the ulterior

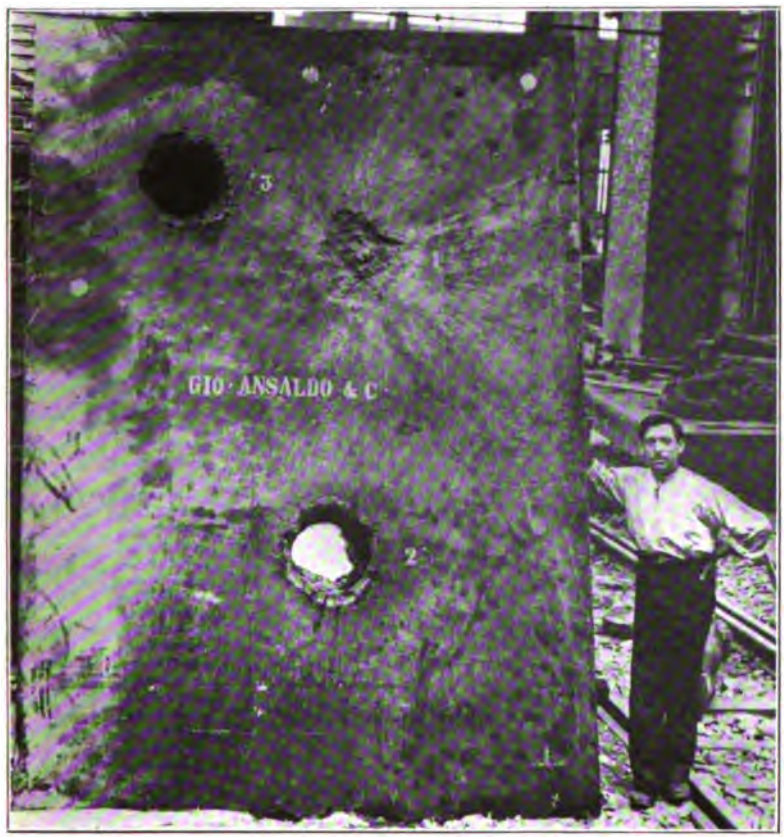

Fig. 16. Armor Plate in which There Is Proper Concentration of Carbon in Surface Strata.

protective efficiency of the plate over an area more or less extended. Such is, for example, the case with the plate [likewise of a thickness of 300 mm (11.8 inches)] for which is shown in Fig. 17 a region struck by a shot under conditions similar to those of the first shot and represented in Fig. 16.

Fig. 17. Armor Plate in which There Is Excessive Concentration of Carbon in Surface Strata.

(28) As to the phenomenon of cracking with "exfoliation" properly speaking, examples are most frequent, and are met with every day in the ordinary practice of the case-hardening of mechanical parts. I will select one for which I have at hand the illustrative material.

In Figs. 18 and 19 are reproduced (with a magnification of about 3.7 diameters) two fragments of the shaft (of soft steel

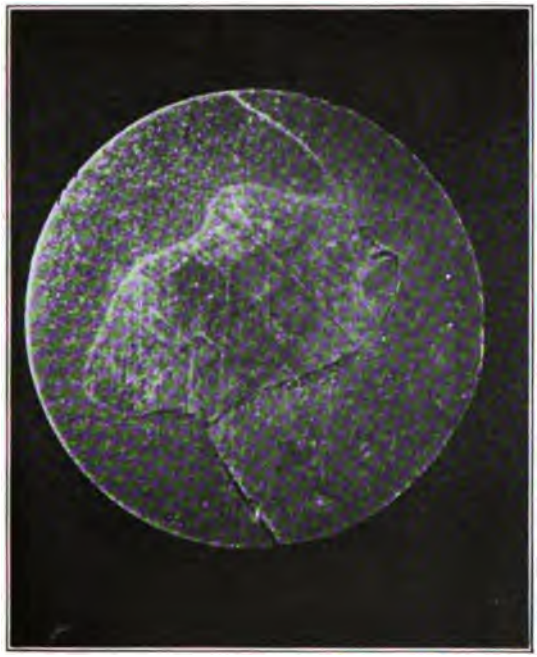

Fig. 18 (x3.7). Fractured Shaft of Rear Wheel of Bicycle. Fracture Shows the Characteristics of Steel Case-Hardened and Tempered.

case-hardened, heat-treated and annealed) from the rear wheel of a bicycle. The appearance of the fracture of this piece—broken in service—is exactly that characteristic of such cracking of steel case-hardened and quenched. The two figures above mentioned show two polished and etched plane sections taken normal to the axis of the piece annealed at about 900°. In both the photographs it is clearly seen that the surfaces of the fracture correspond to a surface over which the structure of the steel varies abruptly.

Such fact is further still more plainly seen in the two photographs shown in Figs. 20 and 21 representing with greater enlargement (60 diameters) two small parts of the line of demarcation between the two zones of different structure of the section reproduced in Fig. 18. From these photo-micrographs it appears plainly that the abrupt variation of the structure of the steel along the surface of the fracture corresponds to a rapid variation in the concentration of the carbon, entirely similar to that

Fig. 19 (x3.7). Specimen from Fractured Shaft of Rear Wheel of Bicycle.

which I have already described in section 16, illustrating the same with the photo-micrographs and the diagrams reproduced respectively in Figs. 1, 2, 3 and 4, indicating their cause and noting that they are, in particular, due to the characteristic action exercised by "abrupt" agents.

As to the mechanical explanation of the fact that the cracks are produced over the surface to which corresponds the sudden

variation in the concentration of the carbon, the fact is obvious. Indeed it is clear that, over this surface, the piece behaves as though it were composed of two distinct parts formed of two diverse metals, which undergo (especially in the quenched condition) diverse deformation as the result of one and the same mechanical stress, and expand in different degree as a result of one and the same variation in temperature. It is to be noted

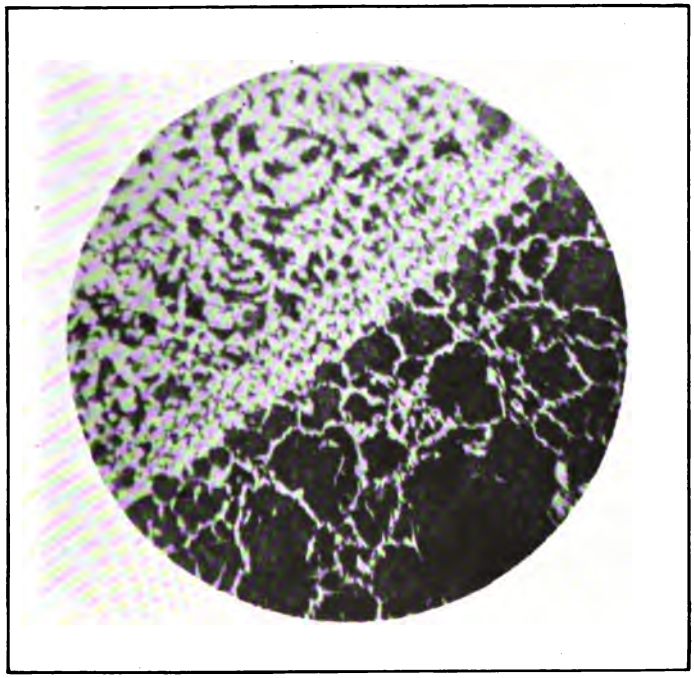

Fig. 20 (x60). Enlargement showing Line of Demarcation between Zones of Different Structure shown in Fig. 18.

that in such conditions the effect of repeated stress (fatigue) is especially evident in the region of contact between the two metals.

(29) Even when the operation of case-hardening is carried out according to the rational rules which I have noted (and in particular with the use of the agent best suited to each special case) no absolute assurance can however be had that a carburized zone will have been obtained possessing precisely the character-

istic properties sought (depth, concentration of carbon, etc.), and of having avoided the many possible sources of trouble, some of which I have already noted. It is therefore desirable to realize some measure of control over the product obtained.

The most definite method of control consists in carrying out determinations of carbon in samples of metal taken from varying depths in the treated zone. This, however, is not applicable (for

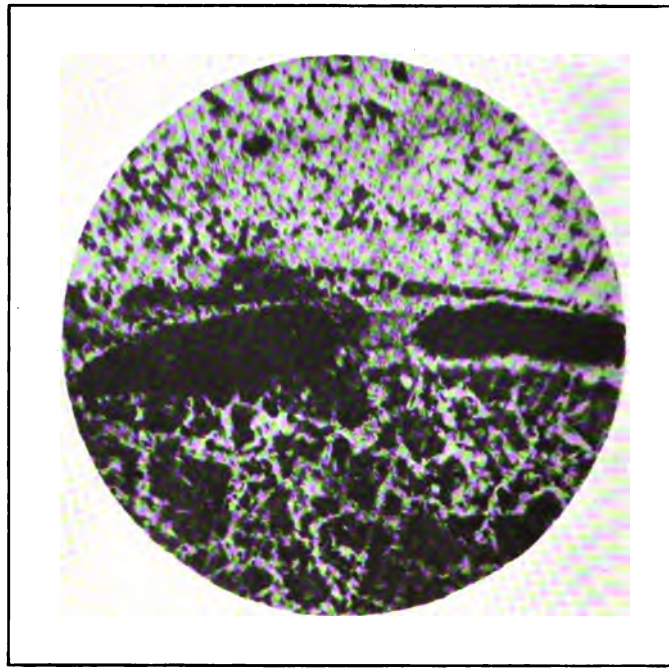

Fig. 21 (x60). Enlargement showing Line of Demarcation between Zones of Different Structure shown in Fig. 18.

obvious practical reasons) except in certain particular cases, as for example in the case of armor plates.

On the other hand, the method most commonly employed, especially in establishments for the treatment of machine parts, is that based on an examination of the appearance of the fracture of parts after cementation and heat-treatment. However, the conclusions which can be drawn from an examination of the ap-

pearance of such fractures (as for example those shown in Figs. 14 and 15) are—for reasons which I cannot here develop—only in uncertain measure reliable. There remains as the most reliable method of control, and applicable to carbon steels or to low percentage nickel steels, the examination, either macroscopic or microscopic, of plane sections taken from the piece after cementation and annealing. Such sections should be carefully polished and etched by a suitable reagent; for example with a 5% alcoholic solution of picric acid, or with dilute solutions of nitric acid.

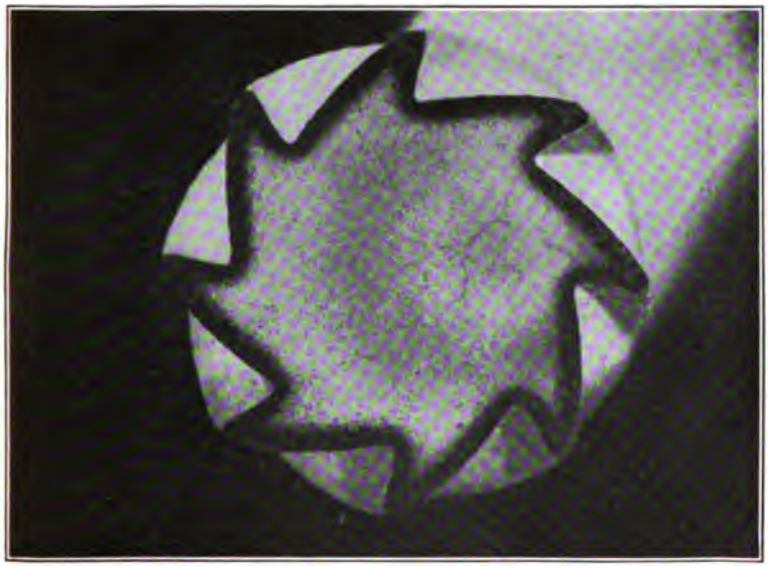

Fig. 22 (x2). Section of Cutter of Soft Steel Treated with a Mixed Agent with Carbon Monoxide Base.

In Fig. 22 is shown, with a magnification of two diameters, a section taken normal to the principal axis, from a cylindrical milling cutter of soft steel, treated with a mixed agent with carbon monoxide base. It is clear that such an examination at practically normal size serves adequately to place in evidence the satisfactory uniformity of the treated zone, as well for the projecting as for the sunken parts of the piece.

More precise control indications may be obtained by means of a microscopic examination of a series of points along the

periphery of such a section, under greater magnification (usually 30 to 150 diameters). We have already seen (Figs. 1 and 2, section 16) how such an examination readily reveals every increase in the concentration of the carbon, and also every abrupt variation of such concentration (see Figs. 20, 21) and permits of distinguishing between a "gradual" and an "abrupt" cementation. This permits also of determining—with greater precision than

Fig. 23. Photo-micrograph of Point of One of the Teeth of Cutter shown in Fig. 22.

with the examination natural size—the grade of uniformity throughout the entire treated zone. Thus from the three photo-micrographs (Figs. 23, 24, 25) it is seen that the carburized zone obtained in the same piece reproduced in Fig. 22, comes from a "gradual" cementation, does not contain an excess of carbon (not exceeding .9% corresponding to the pure pearlite from the external boundary of the zone), and preserves such properties

with satisfactory uniformity in all its various parts—as well on the extreme points of the teeth (Fig. 23) as at the bottom of the spaces between them (Fig. 24), as also in the plane body of the piece (Fig. 25).

It is superfluous to point out that control of the character here noted—not permitting of application to all the pieces treated—is only applied to a certain number of pieces, taken

Fig. 24. Photo-micrograph of Section at Bottom of Space between Teeth of Cutter shown in Fig. 22.

casually from a series treated contemporaneously in the same charge in a pot or furnace.

On all the pieces treated, there are carried out, usually, only tests of surface hardness after heat-treatment. For such tests use is commonly made of the well known methods of Brinell or of Shore. Sometimes one is content with a simple file test.

(30) Before concluding these brief notes I believe it opportune to mention a practical problem which frequently presents itself in the technique of cementation. I refer to the problem of the partial protection of pieces subjected to the process with a view of obtaining, in certain determinate parts of their surface, an exemption from the process. In such pieces it is often necessary to avoid the action of the agent on certain parts of the

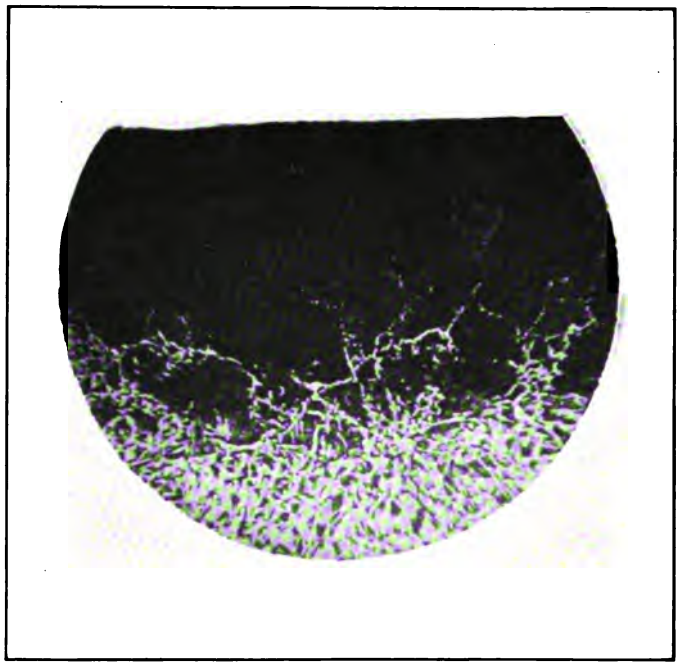

Fig. 25. Photo-micrograph of Body of Cutter shown in Fig. 22.

surface, where the metal is to retain—even after quenching—its strength, tenacity and softness for cutting with tools. The means commonly employed to obtain such ends consist essentially in the application, on the part of the surface which it is desired to protect, of a layer of inert substance. Use is made, for this purpose, of layers of fire clay, metallic covers applied mechanically, layers of metal (copper, nickel) electrically deposited, etc. But these various protecting substances are often of difficult

practical application, and moreover their protective action is somewhat limited, especially when the operation is carried out at a very high temperature.

The problem of an efficient partial protection of the pieces subjected to the process of cementation, is not yet solved in a thoroughly practical and fully satisfactory manner.

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Paper No. 170

METALLOGRAPHY AND THE HARDENING OF STEEL.

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As a contribution on the Metallography of iron and steel to the Engineering Congress I propose to consider briefly the influence exerted by Metallography on the elucidation of the still much debated question of the causes underlying the hardening of steel.

That certain steels can be made extremely hard by rapid cooling from a high temperature, as for instance, by quenching the red-hot metal in water, has been part of men's knowledge for thousands of years. There is no record, however, of any very early attempt at explaining the phenomenon.

Phlogiston Theory.

During the phlogiston period it was held by many that steel was iron that had been loaded with phlogiston by heating it in contact with combustible substances, and that in order to retain in the metal as much phlogiston as possible, thereby increasing its hardness, it was necessary to cool it very quickly, on the ground that slow cooling permitted the escape of some phlogiston with corresponding loss of hardness. It is not without interest to note that this crude conception has at least one point of resemblance with many of the modern theories, namely, the necessity, in order to harden steel, of retaining in the cold, through rapid cooling, a substance or a condition which is normally present in the metal at a high temperature; they called it phlogiston, while it is now described as beta iron, solid solution, amorphous iron, etc.

Percy's Explanation.

The publication of Percy's "Iron and Steel" in 1864 was epochal and his description of the views prevailing at the time

concerning the phenomenon of the hardening of steel is worth quoting:

"In molten, or even in strongly heated solid steel, the carbon is wholly combined, or, possibly, simply dissolved; and by sudden solidification of the metal in the one case, or sudden cooling of it in the other, the whole of the carbon remains diffused through the mass. However, the carbon may have separated notwithstanding, and exist in a state of infinitesimally fine division; and it is conceivable that it may be in the allotropic condition of graphite, and may yet, owing to what I will venture to designate an atomic state of disaggregation, be capable of entering into combination with nascent hydrogen, and produce the residue supposed to be indicative of the presence of what is termed combined carbon. Whether this view be correct or not, it is certain that hard and soft steel differ essentially with regard to the mode of existence of the carbon in the mass.* ..... The particles of hardened steel are obviously in a state of tension, which may, probably, be analogous to the particles of glass in the unannealed state; and, if the former were transparent, the polariscope would, it is reasonable to suppose, reveal a structure similar to that which it renders manifest in the latter."

It is very interesting to observe that many of the assumptions upon which modern theories are based were familiar to Percy, namely, the existence of carbon in a combined and dissolved form (an early conception of solid solutions), the retention by sudden cooling of carbon in a diffused condition and the existence of tension or strains in quickly cooled steel.

Akerman's Compression Theory.

In 1879 Akerman attempted to explain the hardening of steel on the ground that the compression resulting from rapid cooling converted the carbon to the hardening condition (Percy's diffused carbon) in which form it imparts hardness to steel. While the belief in the presence of hardening, i. e., dissolved, carbon in quenched steel is still a very general one, the

* As early as 1822 Faraday showed that the carbon present in unhardened steel behaves differently when subjected to hydrochloric acid from the carbon present in hardened steel: in the former case a carbonaceous residue remains after the metal has been dissolved, while in the latter there is practically no residue left.

conception that its formation is due to the compression to which the metal is subjected on quenching is hardly to be entertained. All evidences, on the contrary, point to the hardening condition being the normal form of carbon above the critical range of the metal and to its being retained by quick cooling, because such treatment denies the necessary time for its transformation into the cement or non-hardening condition stable below the critical range.

Howe's Explanation in 1890.

During the time that elapsed between the publication of Percy's book and that of Howe's famous "Metallurgy of Steel" in 1890, but little progress appears to have been made in solving the problem under consideration. Howe mentions as a probable cause of the hardening of steel, the retention, by quick cooling, of carbon in its hardening form. He writes: "I gave reasons for believing that at or about cherry-redness the carbon of steel passes almost wholly into the hardening state, combining with the whole of the matrix of iron present to form a compound, which, when cold, is intensely hard and much stronger and more brittle than pure iron, and which is preserved by sudden cooling". He also considers the severe strains resulting from the hardening operation owing to "dissimilar rates of contraction" as a possible cause, contributory at least, of the hardness produced by rapid cooling.

Howe also alludes to the "diamond theory", which holds that, by sudden cooling, the carbon present in steel is converted into diamond, an hypothesis hardly deserving consideration.

Early Tension or Stress Theory.

During the days preceding the advent of Metallography it was loosely contended by many that the hardness of quickly cooled steel was due, as already mentioned, to a state of severe tension or stress created by the rapid cooling, owing to the different rates of contraction between the center and outside layers of the quenched piece. The fact that carbonless iron and other metals and alloys cannot be sensibly hardened by rapid cooling, although they also should be under severe tension, does not appear to have disturbed the mental repose of the advocates of the theory; nor the fact that according to their view it should not be possible to harden razor blades; nor again,

the fact that a difference of some ten degrees centigrade in the quenching temperature suffices to produce great increase of hardness at the higher, and complete absence of increase at the lower, temperature.

Osmond's Allotropic Theory.

In 1890 Osmond announced his discovery of the occurrence of two thermal critical points in the purest iron obtainable, from which he logically concluded that iron existed in three allotropic conditions, namely, gamma above the upper critical point, beta between the upper and lower point, and alpha below the lower point. He showed by scientific reasoning of a high order that the hardness of quickly cooled steel might be ascribed to the retention in the metal of some beta iron, a variety which he believed to be extremely hard. Osmond argued that gamma iron was non-magnetic, moderately hard and very difficult to retain in the cold; that beta iron was non-magnetic, very hard and readily retained in the cold metal by rapid cooling; and that alpha iron was magnetic and soft. Since carbonless iron cannot be hardened by sudden cooling and since hardened steel is magnetic, it was necessary to assume that the presence of carbon is necessary to prevent, during quick cooling, the transformation of beta into alpha iron, and that even after quick cooling some alpha iron is present in the metal. The physical properties of manganese steel which is free from thermal critical points and which was found to be—as it should be, in accordance with the theory,—non-magnetic and hard after slow cooling, afforded a striking support of Osmond's theory.

While Osmond's views found at first many followers, some metallurgists doubted from the start the existence of beta iron, and the number of unbelievers has been on the increase ever since. It has been argued that beta iron has in reality no existence, (1) because, as a matter of fact, the second thermal point described by Osmond does not exist in strictly pure iron, a contention which has been definitely refuted by Dr. Burgess of the Bureau of Standards; (2) because of the absence of any crystallographic change corresponding to the formation of beta iron, a view which arbitrarily assumes that an allotropic change must necessarily be accompanied by a change in crystalline

structure; (3) because, except for a change in magnetic properties, no discontinuity has ever been shown to occur in any of the properties of iron at the beta point, an assertion opposed to the findings of several investigators of repute; (4) because while a magnetic change occurs, that change is progressive and does not, therefore, indicate a real discontinuity, a contention which is open to challenge; and (5) because magnetic transformations are in a class by themselves and do not imply allotropic changes.

While in their eagerness to prove the non-existence of beta iron, some writers have stretched their scientific imagination to the breaking point, in summing up their contentions, it would seem that they have failed in their purpose, their attacks having been directed, unconsciously no doubt, against the name rather than against the substance. They are all compelled to admit that between the gamma variety existing normally above the upper critical point and the alpha variety normal below the lower point, the condition of iron between the two points is neither gamma nor alpha—and that, after all, is the main feature of Osmond's theory. Whether instead of being called beta iron, that condition should be described as alpha iron holding carbon in solution, non-magnetic alpha iron, amorphous alpha iron, interstrained alpha iron, etc., does not, as a matter of fact, affect the vitality of Osmond's theory. It remains true that in order to harden steel, the metal must be kept, partially at least, in a non-gamma, non-alpha condition. To call it the beta condition certainly makes for simplicity of speech. If I understand them correctly, these recent theories, without exception, hold that to harden steel we must, through quick cooling, retain the condition existing during the thermal critical range; while some (the stress theories) maintain further that that condition is created by rapid cooling through the range. The former ascribe to rapid cooling the retention only of the hardened condition, the latter its creation as well as its retention. These contentions can readily be reconciled with Osmond's theory.

The Stress Theory Again.

The stress theory was greatly strengthened by André Le Chatelier and others, who argued that the well known expansion accompanying the allotropic transformation of gamma iron into

beta or alpha iron must necessarily result in a severe internal straining of the metal when this expansion is opposed by quick cooling. This reasoning explains satisfactorily why metals which do not undergo allotropic transformation, and in which, therefore, there is no spontaneous expansion on cooling at certain critical temperatures, cannot be hardened by quick cooling, but it does not explain why carbonless iron cannot be hardened.

That hardened steel is generally in a severely strained condition no one denies; that the strained condition contributes to the hardness of the metal may readily be conceded; that it is the sole cause of the hardening of steel through quick cooling is more difficult to accept.

Le Chatelier's Theory.

Le Chatelier has never accepted as probable the existence of an allotropic condition of iron between gamma iron stable above the upper critical point of pure iron and alpha iron stable below its lower point. He prefers to attribute the hardness of rapidly cooled steel to the presence in the metal of carbon dissolved in alpha iron, the quick cooling permitting the transformation of gamma into alpha iron but causing the carbon to remain in solution. In his opinion this state of solid solution is sufficient to account for the great hardness of quenched steel, although alpha iron is soft.

Arnold's Sub-Carbide Theory.

Arnold claims the formation above the critical range of a carbide of iron, Fe_{24} C, containing, according to atomic proportions, 0.89% carbon. In steel with less carbon, the carbide Fe_{24} C forms a solid solution with the excess iron present; while in steel more highly carburized it forms a solution with the excess carbon. The carbide Fe_{24} C is said to be very hard and its retention in the cold by sudden cooling causes the hardness of quenched steel. There are absolutely no evidences supporting this rather fantastic conception, whereas it is opposed by experimental facts as well as by theoretical considerations. It is advocated by Arnold only and by some disciples educated by him.

McCance's Interstrain Theory.

Andrew McCance believes that on cooling steel quickly from above its critical range the whole of the carbon remains in solution while the bulk of the gamma iron is converted into alpha

iron, in this respect following Le Chatelier. This alpha iron, however, according to McCance, is in an interstrained condition owing to the fact that its crystalline units have been denied the time to assume an homogeneous orientation, and the hardness of quenched steel is due to this interstrained condition. It is further contended that, contrary to some recent views, strained iron cannot be described as amorphous because if it were amorphous it could not be ferro-magnetic—"interstrain" being a better term to describe its condition. McCance writes: "On quenching steel, the carbon is retained in solution and in turn it retains a proportion of the iron in the gamma condition, but the majority of the iron is alpha iron. At the quenching temperature the crystal grains had the crystalline symmetry of gamma iron, and the gamma iron retained in the quenched state by the carbon will form an internal network in these original steel grains. The rest of the iron will be transformed, and will form crystal units of alpha symmetry, but these will be prevented by lack of time, by internal friction, and by the gamma iron network, from arranging themselves to form homogeneously oriented alpha crystals.

The alpha iron will be in a condition similar to interstrain, and great hardness will result.

Humfrey's Amorphous Iron Theory.

According to J. C. W. Humfrey, "the hard structure which can be produced in carbon steels by quenching and in certain alloy steels by normal cooling, is due to the presence of a hard amorphous solution of alpha iron and iron carbide, which solution may be compared to Beilby's amorphous phase formed by overstrain.

"To explain the formation of this amorphous phase, the author advances a theory that the passage of a substance from one allotropic modification to another of different crystalline form involves the temporary formation of an amorphous state, corresponding to the liquid phase of the modification about to be formed. In steels such a change occurs at the critical thermal point; and if due to sudden cooling or to the presence of certain alloyed elements, the change point is lowered to a temperature below that at which crystallisation in the viscous mass becomes difficult, then the amorphous form will be retained in a metastable form in the cold".

Carpenter's and Edwards' Twinning and Amorphous Iron Theory.

Carpenter and Edwards argue that in quenching steel very severe internal stresses are set up, causing internal straining of the metal, which in turn results in the formation of numerous twins and of hard amorphous layers. The markings of martensite, in their opinion, correspond to these twins. Edwards writes: "That the material is internally strained is evident from the facts which have been published, namely, the metallic crystals are broken up into an exceedingly large number of twin lamellae. Further we believe that the hardness produced by quenching is brought about by crystal twinning and possibly direct slipping and the formation of amorphous layers as a result of the internal deformation".

Summary.

It will be obvious from the foregoing that the many recent attempts at arriving at a satisfactory explanation of the hardening of steel are based on one or more of the following conceptions: (1) existence of a hard allotropic variety of iron, (2) existence of solid solutions involving the occurrence of so-called "hardening" carbon, and (3) existence of strains in quenched steel causing or not an amorphous condition of the iron.

It will likewise be obvious that no theory so far presented fully satisfies our craving for a scientifically acceptable explanation of the many phenomena involved.

It would seem as if the methods used to date for the elucidation of this complex problem have yielded all they are capable of yielding and that further straining of these methods will only serve to confuse the issue, a point having been reached when this juggling, no matter how skilfully done, with allotropy, solid solutions and strains is causing weariness without advancing the solution of the problem. The tendency of late has been to abandon the safer road of experimental facts and to enter the maze of excessive speculations, in which there is great danger of some becoming hopelessly lost.

The conclusion seems warranted that new avenues of approach must be found if we are ever to obtain a correct answer to this apparent enigma.

Paper No. 171

SYMPOSIUM ON THE METALLURGY OF COPPER.

Edited by

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PROGRESS IN COPPER METALLURGY.

By

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The progress of copper metallurgy is much like that of the amoeba, a thrust forward comes now at one point, now at another, with the net result that the whole body progresses at a fairly steady rate. The conditions to be met change from month to month, and attention is directed now at one set of conditions, now at another. Today when everyone is talking of hydro-metallurgical methods it is hard to realize that a decade ago blast furnace smelting, now largely neglected, was a similarly absorbing topic. At that time the roasting of copper ore was not the fine art it has since become, nor had reverberatory furnaces reached their present stage of development, so that the heat efficiency of a reverberatory furnace was low. Blast furnace smelting, with the ore in intimate contact with the fuel, was so much more efficient and so cheap that metallurgists were confident that it would continue to hold the leading place. The ore deposits then worked and the methods of mining then in vogue produced lump ore and the view seemed justified. Blast furnace smelting developed as mining operations (in most places) penetrated to depths below the oxidized ores, so that the sulphur and iron content of the ore mixture became too

high and the copper content of the resulting matte too low for economical work. Copper metallurgists were clever enough to quickly perceive that if the sulphur and iron could be oxidized in the blast furnace they would furnish heat, thereby doing away with the necessity for an equivalent amount of coke, which is expensive and also, being bulky, displaces ore in the smelting zone and so cuts down daily capacity. In the study of this problem it was not long before an elaborate technology was worked out so thoroughly that, with an ore high enough in sulphur, it was found quite possible to smelt copper ore in the blast furnace without using any coke at all. Many interesting details were the subject of much study. Thus the economy of preheating the blast was discussed at considerable length by metallurgists.

The successful smelting of copper ore in the blast furnace without the use of coke was a notable achievement, and yet the economic advantage was largely nullified by an extraneous circumstance which could scarcely have been foreseen. The period was one of rapidly increasing use of copper, and the geologists and mining engineers were busy in searching for new deposits of copper ores. Large deposits of material containing 25 to 50 lbs. copper per ton, in the form of disseminated sulphides, were available if any use could be made of them. Direct smelting of such ores was out of the question, but in the Lake Superior region ore of a like content had been, for many years, cheaply concentrated. It had not been supposed that such low-grade sulphide ores could be profitably concentrated, but properly directed experiments soon showed that they could, and that with large scale, low-cost mining and milling a good operating profit could be made on the operation. But since no blast furnace could possibly handle the resulting finely crushed sulphide concentrate, roasting and smelting in reverberatory furnaces became a physical necessity. This directed attention toward both these operations and it was soon found possible to reduce the cost of roasting, improve the product, and to increase the tonnage per roaster. Even greater progress was made with the reverberatory, changes in the design increased its thermal efficiency and tonnage smelted, the introduction of boilers into the flues leading away from the reverberatory making a great

saving in the cost of fuel. Crude petroleum became abundant and cheap, through other extraneous causes, and its use as a fuel led to smoother working and cheaper costs in those regions where its comparative cost per ton, plus relative freight costs enabled it to supersede coal. The amount of flue dust made by a reverberatory is very small, and its economy in this regard as compared to rehandling the abundant flue dust made by a blast furnace, coupled with the reductions in operating costs made by the improvements above mentioned, soon put reverberatory smelting almost on a par, in operating costs, with blast furnace smelting, and the latter now no longer enjoys the tremendous lead it so long possessed. Blast furnace smelting, except as an adjunct to reverberatory smelting, bids fair in the future progressively to decrease.

The fine crushing to which low-grade ore must be submitted to prepare it for concentration leaves it in a state of division most suitable for the application of hydro-metallurgical processes, and the tailing from such concentration may therefore be considered as material ready prepared for treatment, on which all costs up to that point have already been paid. This gives an advantage to such processes and much study has been directed toward devising for low-grade copper ores some wet process that in cheapness, efficiency, and completeness of recovery might be at least comparable with the cyanide process for gold. Notable progress has been made already in this endeavor and the advance still continues. Oxidized ores and low-grade ores which have not been subjected to concentration share in the important effect which such a process will have on the treatment of copper ores. All the work so far goes to indicate that the leaching solution used in nearly every case will be a dilute solution of H_2SO_4 and the necessity for an abundant supply of cheap acid may lead to the recovery of the necessary sulphur from the smelter fumes. This would be fortunate for the smelter men, since of recent years they have been increasingly harassed by suits to recover for damages alleged to have been caused by the sulphur content of the escaping gases. Recent tendencies in copper metallurgy have, therefore, been the working of lower and lower grade deposits, the devising of large scale mining operations to reduce the cost, a tremendous

growth in milling in order to reduce smelting costs, the necessary employing of reverberatory smelting, with improved technique, and lowered costs. Along with this has come improved technique in roasting and converting matte, the successful use of basic lining for converters having improved and simplified general smelting operations as well as those of converting itself. Most recent, and still in progress, is the development of local wet processes for the extraction of copper from its ores, and it seems probable that this will have an even more profound effect on the general metallurgy of copper than the other phases discussed above.

DISCUSSION

Mr. Hamilton. **Mr. E. H. Hamilton,*** Mem. Am. Inst. M. E., stated that difficulties arise in practice which do not appear when making experiments. He called attention to the need of utilizing the heat value of the sulphur of the ore in reverberatory practice.

Mr. Ricketts. **Mr. L. D. Ricketts,**** Mem. Am. Inst. M. E., called attention to the difficulties which were encountered in connection with the use of superheaters in reverberatory practice. He stated that a dust loss occurs in reverberatory treatment, notwithstanding assertions to the contrary. This, he said, was confirmed by the work of Mr. Lee at the Copper Queen upon fine concentrate. He also called attention to the difficulty of disposing of the sulphur.

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Paper No. 172

ADVANCES IN COPPER SMELTING.

By

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INTRODUCTORY.

The most notable difference between the practice of copper smelting in the past 10 years and the 10 years preceding is the rapid growth in favor of reverberatory as compared with blast-furnace smelting. Formerly most copper-smelting plants contained only blast furnaces, whereas now such a plant is the exception and the day seems rapidly approaching when the majority of copper-smelting plants will use blast furnaces only for smelting of secondaries, such as matte and slag skulls and cleanings, and the smelting of new material will be done chiefly in reverberatories.

There were several reasons for this radical change:

(1) The lengthening of the reverberatories at Anaconda, together with the semi-continuous mode of operation introduced at that plant, resulted in bringing the cost of reverberatory smelting practically to the level of blast-furnace smelting.

(2) The introduction of oil firing in conjunction with the long furnaces made reverberatory smelting attractive in localities where oil is cheap and coal and coke expensive.

(3) The success of pulverized coal for heating reverberatories has lessened the cost of fuel per ton of charge to such an extent that in many localities the blast furnaces can no longer compete with reverberatories.

(4) Finally the remarkable recoveries which can now be obtained by oil-flotation methods of concentration have made preliminary concentration of ores followed by smelting of concentrates more profitable than direct smelting, even on com-

paratively high-grade material. The concentrates, being very fine, must necessarily be treated in reverberatories.

At Anaconda, for example, it has been decided to stop smelting first-class ore direct, as has been the practice hitherto, and concentrate all of the ore as it comes from the mines. Nothing but fine concentrates will be made, and the blast-furnace plant will be replaced by reverberatories. Large economies will result from this step, due, in part, to the fact that reverberatory smelting with pulverized coal is actually cheaper than blast-furnace smelting, per ton of charge, and, in part, to the elimination of large quantities of barren flux which must be used in the blast furnaces when smelting ore charges.

The success of basic lining for copper converters has revolutionized converter practice in every smelting plant in the country. The cumbersome, unreliable and expensive silicious lining has been replaced practically everywhere by the magnesite-brick lining.

It has been demonstrated that practically any size or shape of converter shell can be successfully lined and operated as a basic converter, from the tiny hand-tilted converters at Gatico, Chile, to the 20-ft., Great Falls type converters used at Anaconda and Great Falls, or the Smith-Pierce type in use at Garfield, Copper Cliff, and elsewhere.

Many of the refinements which it was thought were needed when basic converting was first successfully introduced into practice at the Garfield plant, such as laying the bricks with linseed oil, the use of cast-iron tuyère blocks, expansible converter shells, etc., are no longer considered of vital importance.

It is generally realized that the vital considerations for successful operation are (1) avoidance of too high a temperature, which was first pointed out by Smith and Pierce, and (2) the maintenance of a coating over the bricks, consisting of a basic slag or magnetite. This was observed and commented upon at Anaconda, where basic converter practice as applied to standard converters was first successfully developed within a few months of the introduction of the Smith-Pierce converters at Garfield.

The successful application of the basic lining to the converters at Anaconda led the Great Falls plant to adopt the

same practice. The type of shell used at Great Falls proved admirably adapted to the new lining, and phenomenally long runs were immediately obtained. This type of converter has since been adopted at many plants in preference to the Smith-Pierce type, notably at Cananea and at Douglas in the plants of the Copper Queen and Calumet and Arizona Companies.

No radical changes have taken place in blast-furnace smelting, except the building of the long furnaces at Anaconda by E. P. Mathewson. These furnaces have been a decided success and have greatly increased the capacity of the plant, besides effecting a considerable saving in fuel and labor.

The hot- and cold-blast controversy has died out and the use of hot blast has been abandoned.

The turbo-blower, connected either to a steam turbine or to a motor, has been successfully developed for pressure up to 16 pounds per square inch, and it seems likely that it will ultimately replace the Root's type for blast-furnace air, as well as the blowing-engines now used for converter air.

The McDougall type of roasting-furnace continues to hold its place not only as a roaster, but also as a preheater where the quantity of sulphur is small and it is desired merely to obtain a hot, dry product for the reverberatories. Air-cooled furnaces are used where the sulphur content of the charge is low or where external firing is required, as where the furnaces are used for drying and preheating. Water-cooling must be used when the sulphur content of the furnace charge is high, otherwise the temperature of the furnace will become too great and the calcine will sinter.

It is being realized more and more that furnace charges should be properly mixed where materials of diverse character are being smelted, and bedding systems are in high favor, particularly in localities where the climate permits of out-door beds.

More attention than ever before is being paid to dust losses and efforts are being made to purify the smoke from smelting works as much as possible, both to avoid litigation and to save copper. The bag-house at the Mammoth plant in California has been quite successful, but efforts elsewhere have been toward the application of the Cottrell electrostatic system. This

system has been highly developed by the cement industry, and much work is being done on the process at Garfield, Anaconda and elsewhere. The precipitation units are being increased in size, and voltages have been increased from 50,000 to 250,000 volts. It is generally conceded that the shutting down of the Ballaklava smelter at Coram was not due to the failure of the Cottrell system.

The Hall Process for recovering sulphur from concentrates, by heating them in a hydrocarbon atmosphere, was tried on a large scale at Coram, but so far the results have not been conclusive.

BLAST-FURNACE SMELTING.

In March of 1905 Blast Furnaces Nos. 1 and 2 at the Washoe Reduction Works(1) at Anaconda were joined by building in the center section of 21 feet. This made a furnace 51 feet long by 56 inches wide, having a hearth area of 247 square feet. There were two settlers, each 15 feet in diameter, and the furnace had two spouts. The center section had a bottom of cast-iron plates, which burned through a few days after the furnace was started. The plates were later replaced by water-cooled plates, which proved entirely satisfactory.

The success of this furnace was followed by the joining of Nos. 3 and 4 furnaces in November of 1905, and Nos. 5 and 6 in January, 1906. Finally No. 7 was joined to Nos. 5 and 6 in August, 1906, making a furnace 87 ft. long. The credit for this radical step belongs to Mr. E. P. Mathewson.

The hot-blast stoves(2), which were so much in evidence a few years ago, were abandoned at most plants(3) owing to high cost of maintenance.

At the plant of the Mitchell Mining Company at Guerrero, Mexico, blocks of wood were dipped into a wash of silica and clay to prevent them from burning before reaching the fusion zone, and were used in place of coke, it is stated, with considerable success. The furnace produced a matte running over 50 percent copper.(4) This was also tried by H. F. Collins, in 1901, at Santa Fe Chiopos, Mexico, but 1 part of wood to 5 parts of coke was all that could be used successfully.

Mechanical feeders for blast furnaces[5] were successfully applied at Garfield, Cananea, Tennessee Copper Co.,[6] and in Australia.[7] The Hodges' feeding-car[8] was developed and used at the Granby smelter with success.

An ingenious modification of blast-furnace smelting was tried at the Vulcan smelter, east of Santiago, Chile.[9] The ore treated was a heavy sulphide, and no value-bearing silicious flux was available, without which the highly ferruginous slag solidified in the fore-hearth. To overcome this difficulty, a down-draft furnace was developed and is said to have been a success.

The use of fuel oil for blast-furnace smelting,[10] to replace coke, has been tried at various places, but always for too short a period to demonstrate its commercial and technical value.

N. H. Emmons described a closed top[11] for blast furnaces to be used where the gases of the furnace are required for the manufacture of sulphuric acid. The top was developed at the plant of the Tennessee Copper Company. Water-cooled tops have come into use, particularly where furnaces are operated with a hot top and brick-work tends to give trouble due to heat and accumulation of accretions.[12] The roofs of the blast furnaces at Anaconda are made of water-cooled cast-iron plates.

The development of the blast furnaces at Great Falls[13] and the thermal effect of blast-furnace jackets[14] are described in the Transactions of the American Institute of Mining Engineers.

A paper on the early development and history of the modern copper blast-furnace[15] has been published by E. P. Mathewson.

Pyrite smelting by the Knudsen method has been in operation at Sulitjelma, Norway,[16] for over four years. In the process, the sulphides are oxidized by a powerful air-current in an upright converter, partially melting the charge and causing the metallic sulphides to flow to the bottom. As soon as a small bath of sulphides has collected, bessemerizing commences, which results in the complete fusion of the charge with production of slag and matte. A thick lining of magnesite brick is used in the converter.

Bedding Systems.

The bedding system for copper ores was established at Cananea[18] in 1906. The plant was designed and constructed by Dwight & Messiter in 1906 and later perfected by Cole and Shelby and put in operation in 1908. It proved a decided success and later was extended to include the feed to the roaster plants. The bedding system was adopted at the Garfield smelter[19] and at the Copper Queen in 1906,[20] also at the Tennessee Copper Co.,[21] at the new Calumet & Arizona Smelter, and elsewhere.

Air-Compressing Machinery.

The new turbo-blower for blast-furnace work is gaining in favor. The new plant installed at Mt. Morgan[22] consists of four turbo-blowers for blast-furnace air and three turbo-blowers for converter air, all electrically driven. Each furnace blower is capable of compressing 18,000 to 20,000 cu. ft. of free air per minute to 64 ozs. per sq. in. They are each driven by a 500-volt direct-current variable-speed motor. The three converter blowers have a capacity of 5000 cu. ft. of free air per minute and compress to 12 pounds per sq. inch. They are of the latest Parsons multiple-stage centrifugal type.

A new turbo-blower, for converter air, having a capacity of 35,000 cu. ft. per minute and compressing to 16 lbs. per sq. inch has just been installed in the Smelter Power-House of the Washoe Reduction Works. It is driven by a Parsons turbine rated at 2000 hp. when running at a maximum speed of 3500 r.p.m. It was built by the Ingersoll-Rand Co.

ROASTING.

The multiple-hearth roasting-furnace of the McDougall type has been adopted to the practical exclusion of all other types; while for sintering, the Dwight-Lloyd machine is steadily gaining in favor.

John E. Greenawalt, of Denver, installed his system of down-draft sintering[23] at the Modern Smelting & Refining Co., near Denver.

In the earlier part of the decade, pot-roasting of sulphides came into general use. The Huntington and Heberlein process was installed at Garfield[24] and at many other places. At

Wallaroo, Australia, a modification of the Huntington-Heberlein process was developed by McMurty and Rogers.[25]

In roasting tailings for leaching, at Anaconda, a McDougall furnace 20 ft. in diameter was equipped with two fire-boxes, one on each side, and connected with the third hearth. The arms are air-cooled and so arranged that, if desired, the warm air can be introduced into the bottom hearth. A belt feeder is used.

A cooler for the hot calcines was developed, consisting of a cylinder built of boiler plate, having a slope of ¾ inch per foot and making 10 revolutions per minute. The cylinder is lined with pipes 1 inch in diameter, through which cold water circulates. The calcines enter the cylinder at 350° C. and are discharged at 45° C. About 25,700 gallons of cooling water are required per day when treating at the rate of 80 tons.

The Wedge furnace[26] is of the McDougall type. Its distinguishing characteristic is a central brick-covered shaft large enough for a man to enter. The top of the furnace is used for drying the material to be roasted. These furnaces are built either air- or water-cooled and with or without fire-boxes.[27] Wedge furnaces are used at the El Paso smelter, at the new United Verde Smelter at Clarksdale and at the new International Smelter at Miami. In connection with the new acid plant at Anaconda, two Wedge furnaces are used.

The Herreshoff furnace[28] has been re-designed and has regained some of its old-time popularity. The arms and shaft are air-cooled. The heated air is used in the furnace, thus increasing the thermal efficiency and permitting the roasting of lower-grade material without fuel. A peculiar type of rake, the angle of which varies with its proximity to the center of the hearth, has lately been introduced for the purpose of securing a more even depth of calcine on the floors.

The Dwight-Lloyd sintering machine consists of a series of grates on an endless chain. The ore to be sintered is fed onto the grates, which move continuously over a suction-box, where the charge is ignited by a flame and air is drawn through to roast out the sulphur. A description of the earlier machine is published in the Engineering & Mining Journal.[29] R. L. Lloyd, speaking of his experiences with sintering at high alti-

tudes,([30]) states that at Cerro de Pasco a charge containing 25% sulphur was sintered without trouble. This could not be done at a lower altitude without considerable difficulty.

Wm. Kelly and H. N. Thomson([31]) patented an improved McDougall arm and rake.

At the Great Falls smelter much work was done to increase the output of their furnaces.([32])

REVERBERATORY SMELTING.

The forerunner of the modern long furnaces was reverberatory No. 4 at the Washoe Reduction Works, which was started July 12, 1904. The hearth dimensions were 102 ft. by 19 ft.([33]) It was such a decided success that the remaining furnaces were remodelled on the same lines as rapidly as possible. The following data are of interest:

Furnace	Started	Length of Hearth
1	Jan. 28, 1905	115 ft. 10 in.
2	Aug. 17, 1904	102 " 0 "
3	Nov. 10, 1904	112 " 6 "
4	July 12, 1904	101 " 9 "
5	May 17, 1904	112 " 4 "
6	Jan. 10, 1905	101 " 9 "
7	Feb. 23, 1905	112 " 6 "
8	May 26, 1905	112 " 4 "

The results of experiments at Anaconda with various coals have been published by C. D. Demond.([34])

Fuel oil was used in the furnaces at the smelter of the Arizona Copper Co., at Humboldt, in 1906.([35]) The oil came from California. The dimensions of the furnace hearth were 98 ft. by 19 ft. Each furnace had 9 oil burners, three at the back and three on each side. They were hung on universal connections, so they could be pointed at any angle. From 11 to 19 percent of oil was used, and a matte carrying about 40% of copper was made. Later the side oil-burners were discontinued.

A circular type of reverberatory smelting-furnace was built at the Copper Smelting Works at Kedabeg, Russia.([36]) The hearth is circular and is 29 ft. in diameter. The waste gases pass over a roasting-hearth. These furnaces are heated by oil flames entering in a tangential direction, causing the flames to sweep around the furnace.

The oil-fired regenerative reverberatory-furnace of the Peyton Chemical Works,(37) in the vicinity of Oakland, Cal., was successfully operated.

Reverberatory furnace practice at Cananea has been described by L. D. Ricketts.(38) Coal and grate firing was used from February to August, 1907, but was unsatisfactory. A pulverizer was installed, the fire-box of the furnace was removed and coal-dust firing was then tried. A high temperature was readily obtained, but the ash "blanketed" the charge. Before this difficulty had been entirely overcome, the Mexican government removed the duty on oil for fuel purposes, and consequently the experiments with powdered coal were discontinued and oil firing was adopted.

At the Boston and Colorado Smelter, at Argo, reverberatory slag was cleaned by being treated with iron pyrite. The cleaned slag assayed 0.15% copper.(39) In 1906 the Detroit Copper Co., at Morenci, used a small reverberatory furnace for cleaning slag from the blast furnaces. This reverberatory was fired with fuel oil and flue dust was blown in above the burners.(40) The dust smelted readily, but the corrosive effect on the roof was too great. Experiments were also made by spreading fine concentrates on the slag, with indifferent success. Four wood-burning reverberatories were successfully operated by the Cienequita Copper Company, Chipiona, Mexico.(41) A 50-ft. regenerative furnace was operated at Nijni Tagilsk, in the Ural Mountains, and 70-percent copper matte was made with a 0.75 percent slag.(42)

Pulverized coal for reverberatory matte smelting was first used at the Highland Boy Smelter, near Salt Lake City, by S. S. Sorensen.(43) The experiment was fairly successful but the system was not adopted. Later, a furnace was equipped at Cananea, but here too the system was not adopted for the reasons previously given. It therefore remained for D. H. Brown, of the International Nickel Co., to establish the use of powdered coal for heating reverberatory matte-furnaces on a commercial basis. Brown found that the difficulties encountered by earlier experimenters were due to not grinding the coal fine enough. Leonard(44) makes some interesting comparisons between the efficiencies of powdered coal and of oil. He finds that, taking

the smelting done per B.t.u., in the case of oil, at 100, the smelting done per B.t.u. in the form of powdered coal ranges from 90 to 99, depending on the character of the coal. Bituminous coals develop higher efficiencies, as a rule, than lignites.

On July 1, 1914, No. 8 Reverberatory at the Washoe Reduction Works was started up on pulverized coal. No difficulties whatever were encountered and the results exceeded expectations in every way. The hearth dimensions of the new No. 8 are 20 ft. by 125 ft. During the month of October, 1914, the furnace averaged 500 tons per day and smelted 7 tons of charge per ton of coal. Reverberatory No. 5 is being rebuilt and will be 147 ft. long by 25 ft. wide. It is expected to smelt 650 tons per day, with a slightly better fuel ratio than No. 8. The results of experience at Anaconda with powdered coal are given in an article by L. V. Bender, published in the Trans. of the A. I. M. E.

CONVERTERS.

Two papers ([45]) ([46]) describing converter practice at Anaconda and Great Falls prior to the introduction of basic linings are now only of historical interest.

From August 18, 1905, to Feb. 1, 1906, Chas. Baggaley experimented with a basic-lined converter at the Pittsmont Smelter,([47]) Butte, Montana. The work was conducted under the supervision of Wm. A. Heywood. An 8- by 13-ft. converter was employed, lined with one course of 9-in. magnesite brick. About 1000 lbs. of ore and four to five tons of matte constituted the initial charge. Ore and matte were added from time to time and slag was taken off until sufficient white metal had accumulated, which was then blown to copper.

In 1909 the Smith and Pierce basic-lined converter was put into operation at Garfield.([48]) The converter shell was about 10 ft. in diameter by 24 ft. long and was lined with magnesite brick. The throat of the converter was near one end.

In an article entitled "Great Falls Converter Practice",([49]) Messrs. Wheeler and Krejci trace the development of the upright converter. A description of the 20-foot converter in use at Great Falls and Anaconda is given. Many other articles on basic converting have been published in the technical press during recent years.([50])

The introduction of silicious ore into converters[51] has become established practice, while blowing concentrates[52] into a converter through the tuyères has been used successfully at Cananea.

The mixing of molten converter-slag and flue dust, so that the mixture might be smelted in the blast furnace, was developed at the Copper Queen Smelter at Douglas. The slag and flue dust are introduced at the small end of a revolving, conical drum.

A machine for casting converter copper was developed at Great Falls. It consisted of an enlarged and improved Walker casting-machine.[53] The straight-line copper-casting machine, which has been installed at the Calumet and Arizona Mining Co.'s new works at Douglas, at the Arizona Copper Co.'s plant at Clifton, and in the new United Verde works at Clarksdale, is described in the Engineering and Mining Journal.[54] When the new smelter at Garfield was built, a new slag-casting machine was designed by F. G. Kelley and installed in the smelter. This machine has been used successfully.[55]

R. G. McGregor devised and patented a new ladle skull-breaker[56] which has been installed at the Calumet and Arizona plant at Douglas.

I wish to acknowledge the valuable assistance of Mr. James K. Murphy in the preparation of this paper.

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DISCUSSION

Prof. Hersam. **Prof. E. A. Hersam,*** Mem. Am. Inst. M. E., called attention to the need for published information upon the different basic converter linings, more particularly with respect to the effect of different converter slags upon them.

Mr. Ricketts. **Mr. L. D. Ricketts,**** Mem. Am. Inst. M. E., showed that corrosion of the basic converter lining was not only dependent upon the percentage of silica and alumina present in the slag, but also upon the temperature of formation of the slag.

Mr. Lachmund. **Mr. Oscar Lachmund,**† Mem. Am. Inst. M. E., asked Mr. Laist if, in his opinion, there was greater economy in the use of basic linings when the converters were in use intermittently, particularly with regard to the cracking which arises from expansion and contraction.

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Mr. Laist.

Mr. Frederick Laist,** Mem. Am. Inst. M. E., replied that the advantages of basic linings diminishs with small-scale operation, but he cited experience at the Great Falls smelter, Montana, and at the International smelter, Tooele, Utah, which shows that intermittent operation was possible for long periods of time with basic linings.

Mr. Hamilton.

Mr. E. H. Hamilton,*** Mem. Am. Inst. M. E., stated this his own observations were similar to those of Mr. Laist.

Mr. Addicks.

Mr. Lawrence Addicks**** inquired as to the effect of the war upon the supply of magnesite brick suitable for converter lining.

Mr. Laist.

Mr. Laist replied that California magnesite is available for this purpose but gave only about one half the service of the Austrian magnesite. Chrome brick, he thought, would be less satisfactory. He stated that this difficulty had been overcome by the market affording Grecian magnesite in any quantity that might be desired.

Mr. Ricketts.

Mr. Ricketts pointed out that the advantage of the basic lining as against the cheaper acid lining was its longer life.

Mr. Bradford.

Mr. R. H. Bradford asked what percentage of sulphur it would be necessary to leave in an ore sintered in order that fuel might be eliminated in blast-furnace practice, and, upon the assumption that it would be possible to eliminate fuel in blast-furnace smelting, how the costs of the operation would compare with reverberatory smelting.

Mr. Laist.

Mr. Laist replied that one half of the sulphur of a 33% ore would probably be lost in sintering and that to expel this amount of sulphur would necessitate McDougall roasters to avoid the clogging of the grates of the sintering machines. He further said that, if the sulphur thus lost could be made available as a fuel, the blast furnace could then probably compete with the reverberatory furnace. In estimating comparative costs, he said that only general estimates could be made and that the exact cost depended upon the cost of oil, coal dust and coke. He placed the cost of reverberatory smelting at approximately $1.20 per ton, and roasting in the McDougall furnace at 25 cents per ton. The cost for smelting high-sulphur charges in the blast furnace he considered would amount to approximately $1.00 per ton, and the cost of sintering, from 80 cents to $1.00 per ton. The total for reverberatory practice, including McDougall roasting, would then be approximately $1.45 per ton and for blast furnace smelting $2.00—probably never below $1.75 per ton. Hence, under present conditions, the costs are in favor of reverberatory practice.

Mr. Duschak.

Mr. L. H. Duschak,* stated that, as a result of some experimental work which he had done, he had found that the sulphur begins to distil from pyrite at 625° C and that at 850° the evolution is very rapid, and that at this temperature sulphur continues to be evolved until the first

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Mr. Duschak. atom of sulphur is eliminated. He stated that to sinter an ore high in sulphur it was necessary to avoid vaporization of the first atom of sulphur.

Mr. Addicks. **Mr. Addicks** called attention to the nodulizing of concentrate which takes place in the rotary kiln.

Mr. Hamilton. **Mr. Hamilton** stated that to sinter satisfactorily, the ore must contain at least 16% of sulphur, and that approximately 3% of the sulphur would remain in the product. He placed the cost of sintering at from 70 to 80 cents per ton. He also stated that the relative efficiency of the reverberatory and blast furnace products depended upon the character of the ore. He considered that an ore high in lime or high in copper could best be treated by the blast furnace.

Mr. Lachmund. **Mr. Lachmund** asked Mr. Laist if he had definite figures concerning the power returned to the boilers through the use of the heat of the waste gases of the reverberatory furnace.

Mr. Laist. **Mr. Laist** replied that in the old reverberatory practice, in which 250 tons of ore were smelted per 24 hours, with the consumption of 60 tons of coal, there was returned 450 boiler hp., and that in the new furnaces, smelting 650 tons per 24 hours and burning 96 tons of pulverized coal, there was returned 900 to 950 boiler hp.

Mr. Ricketts. **Mr. Ricketts** stated that 40% of the fuel in oil-fired furnaces was available for the production of steam. He stated that he was less confident of the universal use of the reverberatory furnace in copper smelting practice. He called attention to the fact that the smelting of acid ores in a reverberatory furnace requires extremely fine crushing and intimate mixing in order to avoid liquation and prevent the formation of siliceous crusts.

Mr. Laist. **Mr. Laist** added that, for the smelting of solid converter slag, the blast furnace was to be preferred. On account of the desirability of avoiding the cost of the 10% of coke which is required in blast furnace smelting, he considered the reverberatory furnace preferable for smelting liquid converter slags. He called attention to the fact that, in the smelting of such slags, in order to reduce the copper content of the slag, which is commonly 1.5% to 3%, it is necessary to add additional sulphide. He also called attention to the difficulty which sometimes arises through magnetite contained in the calcines from the McDougall furnaces forming accretions upon the bottom of the reverberatory furnace. This, however, he said, could be overcome by the use of pre-heated concentrate.

Mr. Hamilton. **Mr. Hamilton** stated that better reduction was obtained in the blast furnace.

Mr. Ricketts. **Mr. Ricketts** stated that the metallurgical balance sheet should be most carefully studied and that all unaccountable losses should be investigated. He referred particularly to the constant error sometimes introduced by improperly taken moisture samples. He then asked Mr. F. G. Cottrell regarding the possibility of making fractional separation of certain of the constituents of smelter gases by electrical precipitation.

Mr. Cottrell.

Mr. F. G. Cottrell,* Mem. Am. Inst. M. E., replied that a number of such separations might be possible. He first called attention to the fact that in order that a substance be precipitated, it must be put into the form of a visible cloud of suspended particles of solid or liquid, as the true gases are not affected. For example, if all the sulphuric acid and arsenic are to be removed from the gases, it is necessary that they be cooled below the temperature at which sulphuric acid and arsenic have an appreciable vapor pressure, which for practical purposes is, say, 125° C. In removing less volatile constituents, such as copper, sulphur and lead, the gases may be subjected to electrical precipitation at higher temperatures. In the case that separation is desired between a volatile constituent and a less volatile constituent, the gases are passed through an electrical precipitation unit at a sufficiently high temperature to keep the more volatile constituent vaporized. This precipitates the less volatile constituent. The gases from this unit may then be passed to a second unit, where they are cooled sufficiently to precipitate the less volatile constituents. In this way it is possible to make separations between certain of the metals and the volatile arsenic or acid vapors. He stated that in the East at the present time the possibility of separating lead and zinc fume was being investigated. Mr. Cottrell also called attention to both the mechanical and electrical difficulties which arise through change in the composition of the material being deposited. He also called attention to temperature as a factor determining the dielectric strength of the gases under treatment—the higher the temperature the lower the voltage which would be carried on the electrodes for a given space, or, stated in another way, the farther apart the electrodes should be set for a given voltage.

Mr. Lachmund.

Mr. Lachmund asked Mr. Cottrell if any data were available upon the relative volatility and recovery by electrical precipitation of silver as compared with other metals in ordinary smelting and refining practice.

Mr. Cottrell.

Mr. Cottrell replied that he could not give any quantitative data from memory, but that it was a well known fact that silver was appreciably volatile at the temperature of ordinary smelting and refining furnaces. He referred Mr. Lachmund to the paper by Chas. H. Aldridge on The Treatment of Silver Furnace Fume, presented at the San Francisco meeting of the American Electrochemical Society.

Mr. Wells.

Mr. A. E. Wells, in commenting upon Mr. Rickett's statement regarding the introduction of errors through faulty moisture samples, said that the present method of taking the moisture sample of ores, and especially of wet concentrate, was not entirely satisfactory and might readily be the cause for apparent metal losses in the metallurgical operations. Since mechanical sampling is little used for taking the moisture sample, the personal equation of the individual taking the sample enters in very largely. These errors could, therefore, cause an apparent gain or loss of the metals. He called attention to a specific case of a copper smelter

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Mr. Wells. where there was received daily 1000 tons of concentrate containing approximately 15% of water. For a period of several months the metal losses at this plant showed an increase of 30% to 40% over the normal loss. Elaborate investigation of all the metallurgical operations failed to disclose the cause of the loss. Finally, in investigating the method of taking the moisture sample, it was found that a new man had been assigned to taking the samples and that his sample was in error through the fact that he did not take as much material from the bottom of the car as from the top, so that the moisture contained in his sample was somewhat below the true moisture content of the car. This, of course, would cause an apparent metal loss, which, although the difference was slight, when applied to 1000 tons of concentrate per day, was sufficient to make a large apparent increase in the metal loss.

Dr. Hofman. **Dr. H. O. Hofman,** Mem. Am. Inst. M. E. (by letter), said that a discussion of the paper prepared by a metallurgist who is in charge of the largest smeltery of the world, and who, as seen by the extensive bibliography given, follows the advances made outside of Anaconda, appears superfluous. However, the scale of operations which has become second nature with the author, leads him to discuss blast furnace smelting from this point of view. Anaconda has stopped its blast furnaces because the reverberatory furnace is more profitable. Under conditions similar to those at Anaconda anyone else would do the same, but many less extended plants which have not that abundant and regular supply of ores, and which have to treat raw ores as furnished, coarse and fine, will hesitate to scrap their blast furnace and rely wholly upon the reverberatory furnace. My contention is that in spite of the tremendous progress which has been made in reverberatory matting, the blast furnace, while not as important as formerly, still has its important function.

Paper No. 173

COPPER METALLURGY OF THE SOUTHWEST.

By

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The copper metallurgy of the Southwest may, by the archaeologist, be traced back to prehistoric times; for we find hammers in some of the superficial pits of carbonate mines, indicating that the aborigines had learned that, at a moderate heat, carbonates mixed with carbon could be reduced to metal. Subsequent to that time and prior to the absorption by the United States of those possessions of old Spain, copper was mined, but apparently not submitted to metallurgical treatment. The Ajo Mines in southern Arizona were worked and their ore shipped via the Gulf of California; and metallic copper was extracted mechanically from the ores of the Santa Rita Mountains, New Mexico, now the property of the Chino Copper Co. Not far from these large deposits, are the Hanover Mines whose ores, probably not until after the Gadsden Purchase, were smelted in small adobe furnaces, the remains of which still stand. The Planet Copper Claims, near the Colorado River at the mouth of the Big Williams fork, were quite actively explored and large shipments of ore made to English smelters. In the first volume of the "Mineral Resources of the United States", issued in 1882, the production of copper in Arizona in 1874 is placed at 800,000 pounds. In 1880 it is supposed to have grown to 2,000,000 pounds. Subsequent to that year accurate statistics were forthcoming.

Apart from these primitive efforts, no copper mining seems to have been conducted until the Leszynskys and Mr. Freudenthal opened up the Longfellow and the Coronado Mine on Chase Creek, near Clifton, Arizona. Their operations date back to 1872, when the nearest railway station was over six hundred miles away. They are said to have done their first smelting in

reverberatories. They next resorted to small Mexican adobe stacks, and, by a series of evolutionary steps, created a very ingenious copper-jacketed furnace, built up of troughs cast from their own crude copper. They were still using very successfully such improvised furnaces when I first had the pleasure of visiting their works in 1881, shortly before they sold out to the Arizona Copper Co., a Scotch organization. By that time, however, the mining and smelting of the ores of the Copper Queen group had been under way for some months; and the progress of the copper interests of the Southwest has been almost uninterrupted ever since. It has now reached an annual output of over 400,000,000 pounds.

The introduction of the porphyry concentrates from the Miami and Ray Mines in 1912 and 1913 caused a sudden increase of production from Arizona, and another augmentation may be looked for in the near future, when the International Smelter puts into the market the combined output of the Miami and the Inspiration companies. The concentrates from the Chino porphyries, coming from New Mexico, go to the El Paso Smelter of the American Smelting & Refining Co., and contribute to the total of the United States 50,500,000 pounds of copper a year.

A sketch of the development of the metallurgical plants and processes at the furnaces of the Copper Queen in the Warren District will illustrate the changes made in the copper smelter's art during the last thirty-three years, in the Southwest.

The work on this mine commenced on the 15th day of June, 1880, and a 36-inch iron-jacket furnace was erected to smelt the ore. The furnace was completed and operations started on the 20th of August, with the following results:

1880	Tons of Ore Smelted	Tons of Bullion of 96% Cu. Produced	Percent of Cu. in Ore
August	114.5	33.5	29%
September	579.5	159.	27%
October	801.	210.5	26%
November	616.	143.75	23%
December	748.5	171.5	22%
1881			
January	718.75	146.5	20%

A second lilliputian stack was added, and that insignificant plant turned out for the original Copper Queen Mining Co., from 1880 to 1885, 34,536,000 pounds of copper in bars from 145,000 tons of ore, yielding an average of 11.5% copper.

During this period the Atlanta Claim, adjacent to the Copper Queen, was successfully explored by the Atlanta Mining Co., and the two companies were consolidated as the Copper Queen Cons. Mining Co. The members of the firm of Phelps, Dodge & Co. had developed the Atlanta and they became the controlling interest in the Consolidated Company, and have remained so ever since.

The extended territory yielded more ore and required more furnace equipment, better and more economically designed, to meet the decline in the price of copper. Lake copper had sunk to 10 cents per pound, and 96% bars, such as Arizona was producing, touched 7⅛ cents. The new works consisted of four small stacks, which were soon enlarged to furnaces of 65 in. by 42 in.

Years of prosperity and regular payment of dividends succeeded the active operations of the new company.

The mines of the Bisbee District fortunately yielded an oxidized ore of fusible composition. The loss of copper in the resulting slags was comparatively low, being about 2½ per cent. In the Clifton and Globe districts, where the ores were in great part silicious, as much as 50% of barren flux was required to render them fusible; the slags, even after this dilution, ran from 3½ to 4½ per cent in copper. This fusible furnace mixture secured prosperity to the Warren District.

At that time, the pneumatic method of concentrating matte had not been introduced, and the absence of sulphur in the ore was looked upon as its redeeming quality. Subsequently, its presence came to be appreciated as its saving factor. The proof of this was demonstrated in 1893, when the Copper Queen was obliged, by the increased sulphur in its deeper ores, to introduce the Bessemer converter. The furnace yield on the same ore at once jumped up 1½ per cent, and the copper contents of the Bessemer bars, which was over 99%, fitted them for electrolytic refining.

The first converter plant erected by the Copper Queen Company dispensed with an electric crane, as the quantity of copper to be handled was not large. For a substitute, each cupola furnace was coupled up with a stationary well, from which the matte alone flowed into a tilting well. This receptacle held a charge, which was poured into a converter on a lower level. The capacity of the furnace was estimated to be, as nearly as possible, that of the converter which it fed. The arrangement was simple and worked well while operating on a comparatively small scale; and for a time, while the cost of electrolytic refining was high, it enabled the company to smelt ores of profitable grade in precious metals in a separate stack and converter. But the refining charges steadily dropping, it soon became profitable to convert the total product of the mine into electrolytic copper, though the average ore has yielded only about seventy-five cents per ton of the precious metals.

Before the expiration of the decade which succeeded the introduction of the converter, the enlargement of the smelting plant became imperative, and a site with ample space for further expansion was selected in the Sulphur Spring Valley, twenty-eight miles distant from the mine. The changes in the planning of the mechanical and metallurgical features of the new works are due to Mr. John Langton and Mr. George B. Lee. Their subsequent changes have been made by Mr. Lee's successor, Mr. Forest Rutherford. These changes consisted in the enlargement of the cupolas and the increase of their number, in the substitution for the small converters of the large twelve-foot vertical converters of the Great Falls type, in the abandonment of the acid lining and the adoption of the Pierce-Smith basic bricks, and in the addition of a roasting and reverberatory plant. Some of the records of production on a single lining are surprising.

The most notable alteration in the smelting works of the Southwest has been the replacement, entirely or partially, of the cupola by the reverberatory, as the result of the increased burden of concentrates delivered to the smelters. The Copper Queen Company added three reverberatories to their plant, in

* Mr. Rutherford's article describes in detail the Douglas Works of the Copper Queen Company.

order to handle with less loss and greater economy the large volume of concentrates delivered from Nacozari and the flue dust from their cupolas.

The Arizona Copper Co., in their new works at Clifton, designed by Dr. Ricketts, has eliminated the cupola altogether, and the American Smelting & Refining Co.'s works at Hayden, erected to treat primarily the Ray concentrates, adopted the reverberatory exclusively. The three reverberatory furnaces to handle the whole of the concentrates from the Miami and the Inspiration, now under construction near Globe, will be 21 ft. by 120 ft. As the concentrates to be smelted will contain approximately 40% copper, their production will exceed that of any other Arizona smelter.

The reverberatory was slow in taking its proper place in our metallurgical works, for the concentration of the low-grade porphyry ores of the Clifton District dates back to the eighties, and their production should have been accompanied by the introduction of the open-hearth furnace. But, in fact, this furnace has displaced the cupola only since Pearce, at Argo, and the metallurgist in the northern fields of the Rocky Mountains, have taught us how to increase its capacity, and how economically to utilize the waste heat.

New promising sources of copper may be anticipated from the Tyrone District, treating the ores of the Burro Mountains, and from the Ajo District.

The mines and works referred to are in the southern counties of Arizona and New Mexico. To the north, Yavapai County alone is an important producer, the copper at present coming, to all intents and purposes, exclusively from the Hon. W. A. Clark's famous United Verde Mine. Phelps, Dodge & Co., in the early eighties, had furnaces on the Big Bug, treating ores from an interesting chain of ore masses, which, however, did not seem to be of very great extent; also furnaces and leaching works at the Copper Basin. These were destroyed by fire and not replaced, though the property is now again active and shipping ore. A third group of mines, in which the copper was contaminated with zinc, was worked by the same firm some twenty years ago near Yucca in Mohave County.

A custom smelter—the Humboldt Smelter—on the Agua Fria in Yavapai County, is run independently, and supplies local demands.

The famous Verde Mines, however, are the only important feeders in the north to the copper output of Arizona. They were first very partially explored in the seventies, when one hundred and eighty miles from the nearest railroad. The first company that operated them for a short period did a highly prosperous business on oxidized surface ores, which were rich in the precious metals, but it was not until the mine had passed under the control of Mr. Clark that it was worked with great energy, and its production rose to 30,000,000 or 40,000,000 pounds of copper per year. The old works recently became so dilapidated that a new furnace plant has been erected in the Verde Valley.

The Verde District, outside of Mr. Clark's property, has not heretofore been productive, but at the present time rich ore is being shipped from the property of the United Verde Extension Mining Co.

The extreme northern counties of both New Mexico and Arizona contain a number of promising copper deposits, which, however, remain as yet undeveloped. Strange to say, Nature's exploration on a stupendous scale, when she cut the huge exploratory drift to the depth, in places, of six thousand feet, and now visited as one of the wonders of the world, exposed very insignificant amounts of mineral.

At the present time the furnace equipment of the works either completed or in course of erection in the Southwest are the

Copper Queen Cons. Mining Co. at Douglas, Arizona.
- 10 blast furnaces, 18 ft. and 20 ft. by 42 ft.
- 3 reverberatories, 91½ ft. by 19 ft.
- 7 12-foot converters.
- 16 roasters.

Calumet & Arizona Mining Co. at Douglas, Arizona.
- 2 40-ft. blast furnaces.
- 4 reverberatories, 19 ft. by 100 ft.
- 6 stands 12-ft. upright converters of the Great Falls type.
- 12 roasters.

United Verde Copper Co. at Jerome, Arizona.
- 4 blast furnaces, 27½ ft. by 4 ft.
- 4 reverberatories, 100 ft. by 19 ft.

6 roasters.
5 12-ft. upright converters of Great Falls type.

Arizona Copper Co. at Clifton, Arizona.
No blast furnaces.
4 reverberatories, 19 ft. by 100 ft.
6 roasters.
6 stands 12-ft. upright converters of Great Falls type.

The American Smelting & Refining Co. at Hayden, Arizona.
No blast furnaces.
2 reverberatories, 19 ft. by 112 ft.
8 roasters.
3 converters.

Detroit Copper Mining Co. of Arizona, Morenci, Arizona.
1 large blast furnace.
4 small converters.

Old Dominion Copper Mining & Smelting Co., Globe, Arizona.
The Old Dominion Company has not yet added a reverberatory to its cupola plant, as the volume of concentrates from its small concentrator has been insufficient to economically feed one. Its plant consists of
6 cupola furnaces, of which more than 4 are seldom used.
2 12-ft. converters of Great Falls type, one only of which is retained in blast, and it has, without relining, turned out 43,000,000 pounds of copper.

Shannon Copper Co. at Clifton, Arizona.
3 blast furnaces.
2 stands of converters.

International Smelting & Refining Co., Globe, Arizona.
(to treat the Inspiration and Miami Concentrates)
No blast furnaces.
3 reverberatories.
6 roaster furnaces.
6 converters.

Consolidated Arizona Smelting Co., Humboldt, Arizona.
(Humboldt Smelter)
1 blast furnace (for copper).
1 blast furnace (for lead).
3 100-ft. reverberatories.
3 100-ft. Edwards roasters.
2 stands barrel-type converters.

Fig. 1 shows a flow sheet of the new plant of the International Smelting & Refining Company, now just completed near Globe, Arizona, to handle the concentrates from the Inspiration and Miami properties.

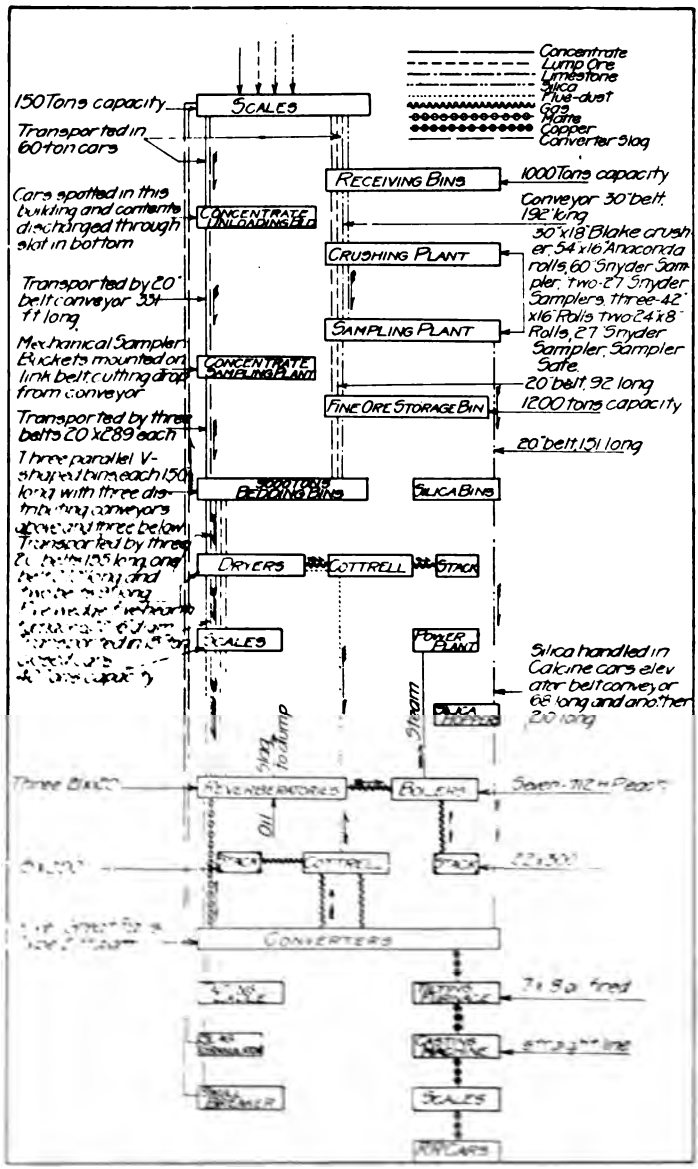

Fig. 1. Flow Sheet of New Plant of International Smelting & Refining Company.

Paper No. 174

REDUCTION WORKS—COPPER QUEEN CONSOLIDATED MINING COMPANY, DOUGLAS, ARIZONA.

By

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In March, 1904, these works, consisting of five blast furnaces, four converter stands, with the necessary equipment to operate them, were started up.

It was immediately found that the plant was not large enough to handle the ore available, so work on additions was commenced and rushed through until May, 1907, when the plant had grown to ten blast furnaces and seven converter stands, with their necessary equipment. Although larger, it still remained entirely a blast furnace proposition.*

The material treated consisted of Copper Queen ores from the Bisbee Mines, concentrates from the Montezuma Copper Company, Nacozari, Sonora, Mexico, and what ores could be purchased from outside mines.

As the Copper Queen ores are very clayey and fall to pieces when dry, the charge for the furnaces was extremely fine (40% of it passing through a ¼-inch screen), the production of flue dust was very large, and, therefore, the losses higher than compatible with good metallurgical work.

To determine what these losses were, a series of tests was started in May, 1909 (a description of which is given in the Engineering and Mining Journal for September 10, 1910), which resulted in numerous changes and additions to the plant. First, the dust chamber was enlarged; second, the converter gases were taken out of the main chamber and delivered to the stack through a separate flue and header; and third, after extensive

* For detailed description, see the Engineering and Mining Journals for August 11th and 18th, 1906.

experiments with the Dwight-Lloyd process, work was started on reverberatory furnaces and roasters.

This addition consisted of two reverberatory furnaces with waste heat boilers attached, six McDougall roasters, flues, dust chambers, and the necessary general equipment.

The idea was to operate one furnace, smelting in it the blast-furnace flue dust, and a part of the Montezuma concentrate calcines, while the remainder would still be smelted in the blast furnaces.

By the time these furnaces were built and put into operation, the ore conditions had changed sufficiently to allow the operation of two reverberatory furnaces, so it was decided to build a third and add three more McDougall roasters. This was done, thus giving us a plant of three reverberatory furnaces and nine McDougall roasters. Again, on account of an increase in the sulphide ores in the Bisbee mines, it was decided to add seven more McDougall roasters, in which to partially roast this material before smelting in the blast furnaces, and thereby give us greater control over the sulphur going to them and over the grade of the matte made by them. This installation will be completed by the end of 1914.

While making these additions and changes to the reverberatory plant, we were also replacing our old barrel type of converters with the vertical converter, or what is generally spoken of as the Great Falls type, 12 feet in diameter, having in the meantime changed over from the acid method of converting to the use of magnesite brick for lining. Seven of these large converter stands were installed in place of eight of the former smaller ones, thus giving us a greater converter capacity without taking up any more space in our building.

Comparing the plant in 1904—which consisted of five blast furnaces, four converter stands, three ore beds, and the necessary power and general equipment to operate them—with the plant as it will be by the end of 1914—which will consist of ten blast furnaces, three reverberatory furnaces, sixteen McDougall roasters, seven large 12-foot converter stands, five ore pits, and the necessary power and general equipment to operate—it is readily seen that the past decade has witnessed a great advancement in our operations, both as to size of plant and method of treating our ores.

Where it could then treat with difficulty 2000 tons per day, it can now treat without any difficulty from 4000 to 4500 tons, and can be run in such a manner that metallurgy and costs can be carefully attended to.

The plant has some peculiar features, most of which are well known; principal among them being, perhaps, the level site on which it is built, which permitted large extensions to be easily made.

The metallurgical treatment of the ores has changed, due to sulphides becoming more abundant and to the fact that oil is available as fuel; the reverberatory furnace process for the treatment of the fine materials has been adopted, while the blast furnaces are used for the coarser material only. The slags made are rather peculiar in the fact that they generally carry from 11% to 13% of alumina, and are, therefore, rather viscous.

The method used to protect the side walls of the reverberatory furnaces is also different from that found in many plants, as practically no barren silicious material is used. At first, this was the case, but it was soon found that with the very basic slags made, it was too expensive to keep the furnace properly fettled with this material, and also that in dropping it through holes in the roof, along the side walls, there was a great tendency to blanket the bath and thereby reduce the smelting capacity of the furnace. A series of experiments was started, which ended in our using, for this purpose, ores running as high as 35% Fe, as low as 25% SiO_2, with sulphur from 15% to 18% and copper about 5%.

It was, of course, impossible to use this class of material throughout the full length of the furnace, because if used too close to the skimming door, some of it was carried out in an unfused state, making the slags too high in copper. We, therefore, lined the front half of the furnace with magnesite brick and did not attempt to clay it at all.

This method, under our condition, seems to work very satisfactorily. In any case, as far as the method is concerned, it is very essential that the ore used must contain enough sulphur to matte all the copper, or otherwise it will stay in the slag in the form of shot and be carried out; whereas, if in the form of matte, it will go through the slag into the bath below, and the slag will be clean.

Paper No. 175

ADVANCES MADE IN THE METALLURGY OF COPPER, GLOBE DISTRICT, ARIZONA.

By

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The greatest advance in the metallurgy of copper in recent years in this district has been in the successful attempt to work the low-grade porphyry deposits owned by the Miami Copper Co. and the Inspiration Consolidated Copper Co. A few years ago it would have been impossible to have worked such deposits, but the great strides made in concentrating methods and the development of highly specialized equipment have made profitable the metallurgical treatment of these low-grade ore bodies. The Miami Copper Co. is already taking steps to increase the capacity of its recently completed concentrator to 4000 tons of ore daily, and the Inspiration Consolidated Copper Co. has in process of construction a concentrator of 7500 tons daily capacity. To handle these concentrates, the International Smelting Co. is building a very complete and modern reduction plant.

Generally speaking, however, the improvement in copper metallurgical practice in this district might be said to have started at the beginning of the present decade. Prior to this time different small smelting plants had been operating in the neighborhood, and the Warrior Copper Co. had made an unsuccessful attempt to leach with sulphuric acid its oxide and silicate ores. Of the smelting plants, those remaining in operation were the United Globe and the Old Dominion smelters. Both were poorly equipped, and owing to lack of railroad accommodation, the receipt of supplies was uncertain. More or less intermittent operating resulted, and the mining and metallurgical industry lacked stability. With the advent of the rail-

road, a marked change for the better took place, but it was not until the Phelps Dodge Company obtained control of the Old Dominion property that a betterment in metallurgical practice started. Hitherto, a lack of sulphide ores in the district had made matte smelting impossible, but with depth, both the Old Dominion and the United Globe mines encountered sulphides. Erection on the Old Dominion ground of a small up-to-date smelter was started. This plant was at first equipped with two 16-ft.-0-in. by 44-in. matting furnaces and two converter stands with four 7-ft.-0-in. by 10-ft.-6-in. converter shells. Since the erection of this original smelting unit, other blast furnaces and converters have been added, until the smelting capacity has been increased to 1500 tons of charge daily. To handle the second-class sulphide ores, a 500-ton concentrator was built, and the concentrates shipped to the new smelter to supply some of the sulphur necessary for the production of matte. Although the matter has frequently been considered, the Old Dominion Company has never deemed it advisable to build reverberatory furnaces, preferring rather to mix the fine concentrates with the coarse first-class ores and treat all in blast furnaces, relying upon adequate dust-chambers to settle and recover the flue-dust produced. Since the completion of this smelter, the actual smelting has been but little changed, and no radical improvement has been made in the methods of reduction.

In the converting department the original practice was to line the shells with barren silica, procured in the shape of quartz boulders from the adjacent hillsides. For a binder, a barren clay was used. Improvement over this practice was made by substituting silicious copper ores from our own mines for the barren quartz and using an aluminous slime from the concentrator for a binder. Later the thought suggested itself that it might be possible to incorporate a certain amount of blast-furnace flue-dust in the silicious linings, and working with this end in view, it was found possible to add as much as 25% of this basic secondary without materially shortening the life of a lining. Thus, not only was a troublesome product taken care of, but the cost of lining the converters was greatly reduced. This practice was adhered to until the early part of 1913, when the acid-lined shells were replaced by a single stand and two

12-ft.-0-in. Great Falls type electrically-operated, basic-lined converters. With this new installation, and using one shell only at a time, it has been found possible to convert all the matte produced, sometimes making over three and one-quarter million pounds of copper per month from a 42% copper matte. This last installation has made necessary many radical changes in the running of the converting department and has also resulted in a decided lowering of costs. One converter has been in continuous use for over eighteen months and has turned out more than 45,000,000 pounds of copper without the expenditure of a single cent for repairs to the lining.

Early in 1912 it was decided to remodel the existing concentrator, first building an additional unit of 500-tons capacity. This addition has just been completed and is equipped with the most recent concentrating machinery. For the recovery of the finer concentrates, the oil-flotation process has been adopted. The coarser product is handled in jigs and over tables and vanners. The preliminary crushing and sampling is done in a new crushing-plant and sample-mill having an hourly capacity of 200 tons. In these two departments, the handling of the ore is as nearly automatic as possible.

Paper No. 176

IMPROVEMENTS IN DESIGN AND CONSTRUCTION OF MODERN COPPER PLANTS.

By

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The Metallurgy of Copper was known at a very early date and the metal has been produced from its ores by crude methods and means by the people of all nations in every age. Copper or bronze tools and implements are among the oldest of the world's instruments, and it has been used for coinage purposes by all nations.

During the past fifteen years there has been little change in the methods used for the reduction of the metal from its ores, except in the improvements of the mechanical appliances for handling the ores and the metal in the various stages of treatment and the greater recovery that is made, due to these improvements and the better knowledge of the processes used.

There is some experimental work going on at the present time in the development of wet processes for the treatment of low-grade ores and the tailings from some of the old mills. Flotation methods are also used, with a degree of success, for increasing the recovery of the values in the slimes.

Improvements are also being made in the design of crushing and grinding machinery of all types used in the preparation of the ores for treatment by these various processes in mills and in the smelter, and thus increasing the recovery and efficiency of the methods used.

The design of modern smelters has been influenced to a certain degree by all these improvements, but the methods employed in the reduction of the ore are about the same, as far as principles are concerned, as in former times. The appliances used are more efficient, the mechanical construction of the fur-

naces is better, there has been a great improvement in the transportation and handling of materials, electric power and compressed air are used in doing more work, and there has been a great development and improvement in machinery of all kinds used in the mining and reduction of copper ores.

Experiments are being carried on to determine the valuable constituents other than copper and the precious metals that are found in the ore and in the gas and flue dust that are incident to the operation of a reduction works.

The moderate success that has been attained in all this work will influence the design of smelters to a great extent in the near future. Additional space will be required for the location of the various buildings required, and the capital outlay will be greater.

Everything is done on a much larger scale now than in the decade preceding the year 1900, due to the general development in all lines of applied science and the increased engineering knowledge, and to the specialization that is applied to the component parts of a large and modern smelter.

Materials are now available for construction purposes that a few years ago were prohibitive on account of their scarcity and consequent cost. Capital is also available in larger quantities, and all these conditions serve to influence, in a marked degree, the design and construction of the modern plant.

The smelter of today is the result of the united efforts of a number of men banded together in an organization, among whom are experts and metallurgists who are specialists in their respective lines.

The Washoe smelter at Anaconda, Montana, in all probability was the first of the great modern plants that was built according to modern methods, by a corps of trained men and skilled engineers who were specialists in construction.

The design of the plant was the result of the experimental work that had been done in the old plants at Anaconda, Butte and Great Falls, Montana, during the previous decade, which had shown what might be accomplished in a plant designed and built so that all departments were so coordinated that the entire plant was practically a machine which performed its work efficiently and economically. A great amount of capital was also

available, so that the work could be done as well as human ingenuity could devise.

The concentrator was designed according to a flow sheet that embodied the results obtained in the experimental work that was done in the old concentrators in the Butte district.

The machinery used in each of the departments was designed, by the engineers in charge of the work, to suit the requirements and conditions, or was made by manufacturers whose machinery had been given a thorough test in the old plants. Larger units were required in each department, and where manufacturers could not furnish them, new designs were made, either by the engineers in charge or by the manufacturers themselves in consultation with the engineers of the company. The application of these large units in the old plants could not be made effective because of the limitations existing in them, but their value, advantages and possibilities were easily recognized when they could be coordinated and arranged in a new plant.

These considerations applied to every department in the smelter. The McDougall furnaces used in the roasting or calcining department had been designed, built and tried at the old works in Great Falls, which has always been to the front in this line of work. The engineers were familiar with the results that had been obtained in the small Herreshoff turret-type roasters in the old plant of the Montana Ore Purchasing Co.'s plant in Butte, and the advantages of a larger furnace of the same type were easily calculated.

Orders were given the engineering department of the company to design furnaces twelve feet in diameter, and after the first preliminary plan was made for that size, the management determined to build furnaces sixteen feet in diameter, air-cooled and with eight hearths. These did not prove successful in operation at first, because the engineers did not fully understand the conditions, having no data on which to base their calculations, and the arms and shafts that stirred the ore on the hearths and came in contact with the heat generated, were not suited for the service and the heat they were obliged to withstand. The trouble was easily remedied by substituting water-cooled arms and shafts, but owing to the greater space required for the new arms and shafts, the number of hearths was reduced from eight to six. The fur-

nace as altered proved successful and was embodied in the design of the McDougall plant at the Washoe works. The furnace was named McDougall after the original patentee of the turret-type furnace, and the improvements made in the design were patented by Messrs. Evans and Klepetko.

The type of reverberatory furnace that became a component part of the new plant was one that had been developed at the Colorado plant in Butte and copied later at the Butte and Boston plant. The furnace was 20 by 50 feet, inside measurements, and was the largest furnace in use in those days. It proved successful, but its capacity was limited, to a certain extent, because the material could not be delivered to it as fast as required. This was taken into consideration in the new plant, and the development of reverberatory furnaces has proceeded along progressive lines, until today the largest furnaces ever built are in use at the Washoe plant.

The type of converter selected for this plant was one that had been tried at the Butte and Boston Smelter, but this was a small unit 7 feet in diameter and 10 feet 6 inches in length. Larger units were required, so they were made of the same type but 8 feet in diameter and 12 feet 6 inches long.

The blast furnaces selected for the new plant were of the type that had been developed at Great Falls, where a great deal of experimental work had been done with different sizes of furnaces. The size finally adopted was a furnace 56 inches wide and 15 feet long, as that had been found to be the size best adapted to the work there.

Having all the component parts of the plant selected, the problem of the engineers consisted in properly coordinating these units in a logical arrangement, and in designing proper appliances for handling the materials to and from the various units.

The segregation of the different departments was adopted because of the magnitude of the operation to be carried on in the plant and to provide room for extensions to the different departments. This policy has been justified by the development that has taken place and by the extensions and increase in capacity that have occurred from time to time.

Segregation of units has not been embodied to such an extent in the later designs as was the case in the Washoe plant, owing

to the different conditions existing at the various locations, and in the ores to be treated.

Nearly all the large companies have, within the past few years, either remodeled their old plants or built new ones.

Since the Washoe plant was built and started in 1902 the following companies have built new plants, and many of them have made extensions within the past five years.

	Capacity Tons
Cerro de Pasco Mng. Co., Cerro de Pasco, Peru	2,000
American Smelting & Ref. Co., Garfield, Utah	4,500
American Smelting & Ref. Co., McGill, Nev.	2,500
American Smelting & Ref. Co., Hayden, Ariz.	800
International S. & Ref. Co., Tooele, Utah	1,200
International S. & Ref. Co., Globe, Ariz.	800
Calumet & Arizona Mng. Co., Douglas, Ariz.	3,000
Copper Queen Con. Mng. Co., Douglas, Ariz.	4,000
Arizona Copper Co., Clifton, Ariz.	800
United Verde Copper Co., Clarkdale, Ariz.	3,000
Granby Con. Mng. Co., Anyox, B. C.	2,000
Mason Valley Mng. Co., Thompson, Nev.	1,000

Capacity is given in tons of ore in one day, and is approximate only. The production of copper is not always in proportion to the tonnage of ore, as some of the plants treat concentrates only, or they are a large portion of what they do treat.

The units in all of these plants are very similar to each other, varying to suit the conditions peculiar to their location. The similarity has been made possible by the exchange of information among the metallurgists and engineers in charge of the various plants. The units are made up in combinations to suit the local conditions which make each and every plant a little different from the other. They represent, in a measure, the ideas of the engineers and metallurgists immediately in charge of the work. Theirs is the privilege of stating what they want and the equipment they desire, and it is the duty of the engineer to whom they delegate the work of designing the plant to meet their wishes as far as may be possible without seriously interfering with the proper solution of the problem.

The time may come when a corps of specialists in all branches of the business may consult together and determine what is the

best solution of the problem or the best plan to adopt; but, heretofore, the design of the plant has depended largely on the ideas of the man who is at the head of the enterprise, either as owner or manager. There is no doubt that the preliminary work in the development of the plans for a large reduction works would be slower, and possibly more expensive, than if one man had the full responsibility; but there is no question that the work would be better and the plant more efficient, if sufficient time were given a commission of experts to consider the problem as a whole and pass on the merits of the plans proposed. The execution of the plans may well be given to one man who will be the executive head and be responsible for the execution of the plans.

In every modern plant there is a sampling works for the purpose of automatically sampling the ore as it is received, and a crushing department for crushing the ore to sufficient fineness for treatment in a reverberatory furnace. This sampling is very necessary, if the recovery that is obtained in the plant is to be accurately determined.

Belt conveyors enter into the transportation of ore between the different departments. The idea is to make the handling of the ore a continuous operation, wherever possible, as intermittent handling of the ore by means of car systems requires heavy equipment and considerable handling. The ore to be treated is only handled in cars where the necessity of transporting it long distances exists, or where the material is such that it cannot be handled on belts without excessive wear and tear. The ore is transported from the mines to the smelter in cars that hold from fifty to sixty tons and is unloaded into bins, constructed of steel, with proper divisions for keeping each class of ore separate, as required. From these bins the ore is delivered to the sampling works by means of conveyors, with 30-in. belts, to the main crushers, where it is crushed to about four-inch cubes and is then conveyed to the top of the sampling mill. The ore passes through an automatic sampling-machine that cuts out ten per cent or more, as required, for a sample; the reject passes through a revolving trommel, or screen, and the fines are taken out and returned, by a conveying belt, to a compartment in the storage bins provided for that purpose, or to a storage bed for fine material, if a bedding system is used. The storage bins are provided

with several compartments, so that, if necessary, various kinds of ore can be kept separate.

If all the ore is to be treated in roasters and reverberatories, it is crushed, in successive stages, until it will pass a screen with three-quarter inch holes or less, if required. If the ore is to be treated in blast furnaces, no further crushing is necessary after the preliminary crushing, and the ore is delivered to storage bins or beds by means of conveyors.

The ten percent that was cut by the first sampler passes through a second crusher and the product is then cut by a second sampler, twenty per cent being the sample, and the reject is returned to the storage bins or beds, as required. This operation is repeated twice more, so that for every ton of material that enters the plant, the final sample that enters the sample safe or bin at the mill is 1.6 pounds.

All the smelters that have been constructed recently have been built as custom plants, so that sampling and crushing plants are essential to making the proper returns to the shippers; and they are arranged so that the representatives of the shippers can see the sampling of the ore, and get duplicate samples if they desire. The work is all done by automatic machinery, so that the results obtained are as nearly accurate as human ingenuity can devise, considering that it must be done economically and efficiently.

The ore is all weighed before unloading into the receiving bins, and, as it is returned to the storage bins or beds, is weighed on automatic-recording belt-weighers, which register the weight of the ore to within one half of one percent. They are simply used as check weighers, as the material is all weighed again before going to the furnaces.

At the works of the Calumet and Arizona Mining Co. and the Arizona Copper Co., two plants recently built, the ore must all pass through sampling mills before treatment in the furnaces. Both these plants are equipped with bedding plants that are primarily intended to mix the ores in proper proportions for treatment in the furnaces, and at the same time, to provide large storage capacity. The Calumet and Arizona Mining Co. has three beds for fine ores for the reverberatories and three, of the same capacity, for the ores that are to be treated in the blast

furnaces. The capacity of each of the beds is 8000 tons. It is necessary to have three beds in order that the work may be carried on continuously, one bed being reclaimed, one completed, and one filling. At the Arizona Copper Co.'s plant they use reverberatories only for smelting, and they have only three fine-beds of 4000 tons each.

The ore is distributed in even layers on these beds by Robins automatic ore-bedding trippers. These beds are made up of the proper ingredients to make a uniform smelting charge. By this means the metallurgist can calculate accurately, from the results obtained in the sampling mill, the amount and kind of ores and fluxes that should be put on the beds in order to provide a proper smelting charge.

When the bed is partially completed, calculations are made to determine what is in the bed, and what more may be required to make it suitable for the furnaces, and the necessary ingredients are added, so that when the bed is finally completed the ore is ready for delivery to the furnaces. The ore is reclaimed by means of Robins-Messiter reclaiming machines, which remove the material simultaneously from all parts of the cross section of the bed and deliver it to conveyors, which carry the ore to the bins at the furnaces.

The fine ore is delivered by means of conveyors to the roasters, located in the roaster building. Above each roaster there is a steel bin that holds about ninety tons of ore, or sufficient for one day's run of the furnace. The ore is delivered into each of these hoppers or bins by conveyors and Robins automatic trippers.

In most of the plans built previous to 1910, the car system is used for the transportation of concentrates or fine ores from the storage bins to the roasters; but in the plants that have been built since that time, belt conveyors are used for that purpose. This permits a very much more compact arrangement in the plant, and the expense of elevating ore by means of conveyors is very small. In the use of the car system, it was necessary to utilize a site where gravity entered largely into the transportation of material, but now, with the use of the conveying system, the roasting plant can be located within convenient distance of the storage bins or beds.

The roasters that were installed at the works of the Calumet

& Arizona Mining Co. and the Arizona Copper Co. are air-cooled Herreshoff furnaces, 21 ft. 6 in. in diameter with six roasting hearths and one drying hearth on the top. The center shaft is made in sections and is 42 in. in diameter, the outer shell of the hollow shaft being cast iron, which supports an inner tube of sheet steel. The cooling air is forced into this inner tube from the bottom of the central shaft, and is at once delivered into the arms in multiple. The arms are cast with an inner partition, which causes the air to circulate through the arms and out into the annular space between the outside shell of the shaft and the inner tube and finally discharge at the top of the center shaft; or there are covers on the cast shaft that can be removed, and the air will then be discharged onto the lower hearth, to assist in the combustion of the sulphur in the ore, if the sulphur is low or the combustion is slow. The air is delivered to the furnace under pressure, and is supplied by fans direct connected to electric motors. The air is positively circulated through the vertical center shaft and the arms.

The arms and rabbles are made of cast iron, the rabbles being attached to the arm by a cast projection that fits into a tapered groove on the under side of the arm. The projection on the rabble is round, and between each rabble there is a filler introduced to fill the space between the projections, so that the rabbles are maintained at a proper distance from each other. There is also another projection cast on the top of the rabble that permits the rabbles to be set at varying angles, so that the flow of the ore over the hearths is of a uniform section.

At some of the plants, Wedge mechanical furnaces are being installed. At the United Verde Copper Co.'s plant the furnaces are 21 ft. 6 in. in diameter and are air-cooled, with the same number of hearths as in the Herreshoff furnace. The principal difference between the two types of furnaces is in the design of the mechanical details.

The hearths in the Herreshoff furnaces were built of common red brick of good quality, but those for the United Verde Copper Co. are made of reinforced concrete, and some of the furnaces at the Arizona Copper Co.'s plant have had the brick hearths that were first installed replaced with reinforced concrete. The probabilites are that all the furnaces built in the

future will have reinforced-concrete hearths, as they are proving satisfactory in operation.

The roasters make considerable flue dust as they treat the fine materials in the plant, and the constant rabbling or stirring causes considerable dusting. This is also true with the blast furnaces, due to the fine material that is in the charge and the disintegration of the ores. The first extensive dust chambers built of structural steel and brick were built at the Washoe plant, but they were of small capacity for the amount of gases they had to handle and it was soon found necessary to build large flues, with portions of the flues widened so as to increase the cross section, thus reducing the velocity of the gases. Dust chambers are now built of structural steel, with large cross sectional areas and with either steel or brick bottoms. They are built above the ground so that the dust can be drawn off into cars. The dust chambers are among the largest units in the plant, and the interior is filled, or partially filled, with baffle plates, or partitions, and wires.

Considerable experimental work is being done at different places in the use of electrical methods for the precipitation of dust. The Cottrell system is being installed at Globe for the precipitation of dust resulting from the operation of the roasters and converters in the International plant, and also at the American Smelting & Refining Co.'s plant at Garfield for the precipitation of dust made by the converters.

In the future a combination of the two methods may be the system adopted, depending on the success of the Cottrell system. The large chamber is effective up to a given point, and is not very expensive when built as it is at the present time.

In connection with these large flues and dust chambers, large chimneys are built for the disposal of the gases and to provide the necessary draft for the furnaces. Several types of chimneys are used, reinforced concrete, common brick, special brick, and steel plate, lined with brick or unlined, depending on the conditions existing at the different plants. Steel-plate chimneys have a four-inch lining of common brick, supported on angle irons about 12 or 14 feet apart. They are more economical in first cost than any of the other types, with the possible exceptions of common brick or reinforced concrete under certain conditions. The United Verde Copper Co. has a steel chimney with a four-inch

lining of brick, 30 ft. inside diameter, and 400 ft. high. The chimneys are usually built close to the dust chambers, and are located so as to serve the different departments with minimum length of flues. In some cases individual chimneys are built for each department.

Smoke damage is a problem that requires a great deal of study in the design of modern smelters, as it is the cause of a great deal of litigation between the companies and the surrounding agricultural interests. As a rule, the smelters are so located that the damage from this cause is provided for, either by the purchase of the surrounding agricultural lands, or by the installation of acid-making plants, or by building tall chimneys so as to diffuse the gases over as wide an area as possible. Most of the modern smelters are located where the surrounding country has but little value as agricultural land. The sulphur in these gases may be utilized in the near future for making acid which can be used in making fertilizer, wherever it is commercially profitable to do so. At some of the smelters there may be built acid plants for the manufacture of sulphuric acid, which will be used for leaching purposes in some of the wet processes that may prove commercially profitable.

The improvements in the construction of reverberatory furnaces in the past decade have been, the increase in length and width, changes in the mechanical details of construction, the use of larger brick and heavier roofs, the distribution of the fettling material for the preservation of the sides of the furnace, and the utilization of the waste gases from the furnaces for the generation of steam. Direct coal firing in these furnaces is being supplanted by the burning of fuel oil, wherever available in large quantities, and where the price compares favorably with coal. The furnaces that are built at the present time are 100 ft. or over in length and from 19 to 24 ft. in width. Where coal is the cheaper fuel, pulverized coal is used to fire the furnaces and will undoubtedly supplant the oil fuel now used so extensively.

Brick bottoms have been tried in some of the large matting furnaces, but with only a degree of success, and the probabilities are that they will not be used very extensively, on account of the first cost of a brick bottom and the danger of losing the bottom. Silica bottoms, as a rule, are more economical and satisfactory.

Still larger furnaces are projected with pulverized coal as fuel, furnaces as long as 175 ft., with the ores charged along the sides of the furnace, and designed so that there will be a continuous flow of slag, the same as in blast-furnace practice.

Over fifty percent of the fuel value in the coal or oil used in the modern furnaces is recovered in the waste-heat boilers that are installed with these large furnaces. They are installed at present with a flue or combustion chamber between the furnaces and the boilers, so that the gases can enter either of the battery of boilers from either of the furnaces, and are so arranged that either boiler can be cut out of service.

The resulting economy from all these improvements has been largely instrumental in the wider application of the reverberatory furnace to the treatment of ores, in recent years, and it is quite probable that blast furnaces may be dispensed with altogether in the future, except where the conditions warrant their particular use.

The improvements made in blast furnaces in recent years have been along the line of increase in size, both in width and length. There seems to be no limit to the length to which furnaces may be built, other than mechanical limitations; they have been built up to 87 ft. in length, and others to 7 ft. in width, but the trend of furnace building indicates that a width of four feet and a length of about forty feet is a desirable size. Such a furnace will treat over one thousand tons of charge in 24 hours. The improvements in construction of mechanical details consist of making the jackets of a furnace in one length, instead of in two tiers, which was the accepted design heretofore for large furnaces. The width of the water jackets has been reduced, so that they may be made strong like a built up girder, and so give added strength to the sides of the furnaces. The jacket extends from the bottom of the crucible to the charging floor girders. They are 17 ft. long and 3 ft. 4 in. wide. Steel plates can now be secured large enough to make any practicable size jacket required, and the development of the oxy-acetylene method of welding permits the welding of the corners of the jackets of any thickness of steel that may be required.

The usual practice, previous to the past few years, was to build the tops of the furnaces of structural steel and brick, but

in the most recently constructed plants, the furnaces are built with air-cooled tops having no brick work in the tops of the furnaces whatever. The only brick used is in the crucibles, and these are chrome brick. The superstructure of the Calumet & Arizona furnaces is built entirely of plate and structural steel, with an air space between the steel plates, and provision made for the circulation of air at natural draft pressure. Provision is made for the expansion and contraction of the interior plates, so that the top can not be distorted due to the heat of the furnace. The large charging doors required on these furnaces are built up in the same manner. These doors are over 22 ft. long and 3 ft. 6 in. high and have shown no indication of warping or twisting out of shape.

At the United Verde Copper Co.'s plant the tops of the furnaces are built up with a system of air pipes, arranged as U pipes, through which the air for the furnaces is forced, thus utilizing the waste heat from the furnaces to heat the air required for the blast. The benefits derived from doing this have not been fully demonstrated, but at the old plant, it has been done for some years, and it is claimed that there is economy in doing it that way. Theoretically, there should be economy in doing it, but the first cost of the furnace is greater and the repairs may be more, due to the added complication; and the power cost may be greater for the air, due to the increased friction in the air passages.

There have been some improvements made in delivering the ores to the blast furnaces, and in all the modern plants some mechanical system is used for delivering the ore rapidly and efficiently to the furnaces. The furnaces have large capacity; consequently, the means for feeding them must be adequate in order to get the best results.

The charges are usually made up at the storage bins, weighed into scale hoppers located at the chutes of the bins, and then dumped into the charge cars; or the charges are made up from the bins by weighing the charge cars on the scales located in the tracks and then loading the required amount of ore into them.

The charge cars are hauled to the furnaces by electric locomotives and the charge dumped into the furnaces. The bodies of the cars are hinged, so that either side may be lifted by means

of air hoists until the proper angle is reached and the charge slides into the furnaces. Sometimes other types of cars are used in which the bodies of the cars roll over and dump the charge into the furnaces.

The coke required for smelting is loaded in the same manner, or is delivered to the charging platform of the furnaces in railroad cars and the coke unloaded into large buggies and charged into the furnace.

At the Calumet and Arizona plant the method of charging the furnace is new and unique. The ore and coke bins are located on the charging floor, and above it, so that the material will drop through openings in the bottom of the bins into the charge cars. These bins are filled by means of conveyors from the bedding system where the ores have been properly mixed ready for charging the furnaces.

The gates in the bottom of these bins are air operated, and so are easily manipulated. The large charge cars stand on scales located in the floor, and the man who has the work in charge loads into them the ore or the coke, as may be required. These cars have four compartments, so that the amount placed into each compartment will be the amount required in the section of the furnace that it is supposed to serve. After the car has been loaded, it is moved forward and dumped into the furnace. The bottom of the car is on a 45° slope, so that as soon as the doors are released by the operator, the charge drops into the furnace. There are four cars to each 40-ft. furnace and they are alternately loaded with ore and coke. The car is electrically propelled. There are four large doors to each furnace and they are operated by compressed air.

Another unique feature in the construction of these furnaces is the method of supporting the side and end jackets. The pressure on the sides of these furnaces is considerable and they must be supported in a strong and substantial manner, and in such a way that the jackets can be readily removed in case of repairs to the furnace. The side of the furnace is supported by a built-up plate girder which becomes the lower side of the bustle or main air-pipe, thus using a minimum of space for supporting the jackets and permitting their removal when necessary for repairs.

From this heavy girder, and also from the girders at the top of the furnaces, screw jacks are provided, and they are connected to the top and center of the jackets, the screw adjustment permitting the securing of the jackets in a strong and substantial manner.

The resulting matte and slag from the blast furnaces flow to large settlers; and the slag flows out at the top, in a continuous stream, into ladle cars holding from 20 to 25 tons. When the cars are filled, they are hauled to the dump by means of electric locomotives. The slag from the reverberatories is skimmed into similar cars and handled in the same manner. In the modern plants, this is the method of handling the slag, with the exception of the plants that are located near an abundant supply of water, when the slag is granulated. This method requires a great deal of height for a slag dump, but, where the conditions are right, is undoubtedly the cheapest; however, the large slag car is the best solution of the problem in most cases.

Quite a little experimental work has been done in trying to recover the heat in the slag and use it in the generation of steam or the heating of air, but little has been accomplished in a commercial way. A molten condition of the slag is an essential requirement in the disposal of slag in large slag cars and in the economical building up of a large slag dump, and consequent economy of operations. Where the converter plant is segregated, as at the Washoe plant, it is necessary to transport the matte in large ladle cars to the converters and pour the matte into them by tilting the ladle. This method increases the amount of skulls made, because of the cooling of the metal while in transit and the delays incident to the system. In all the modern plants, the converters are located in a building adjacent to the furnace buildings and served by cranes that handle large cast-steel ladles that hold 20 tons of matte, into which the matte is tapped directly from the furnaces. The ladles are transported to the converters by cranes and the contents poured into the converters.

The improvements in the design of converters have been along the line of increased capacity in both types, cylindrical and vertical, that are most in favor in the large plants. Cylindrical converters are built as large as ten feet in diameter and twenty-five to thirty feet in length, and vertical types are built twenty

feet in diameter, with about the same capacity of charge as the cylindrical type. They are made possible by the development of the improved linings used, and also by the improvements in the methods of converting.

Magnesite brick are used for the linings in all the modern plants. The brick are much cheaper now than when the first experimental work was done along this line. Experiments with this lining have been conducted by different metallurgists for over twenty years, but it is only recently that it has been made a commercial success. The metallurgy of converting is far better understood at the present time, and also the practical operation.

Silicious ores are treated in considerable quantities in the process of converting, and the methods of getting it to the converters have been improved considerably.

In the most modern plants, bins are located above the converters, into which the ore is delivered by means of conveyors. From these bins, spouts deliver the ore directly into the converters by gravity. These spouts are so arranged that when the converters are in operation they can be moved out of the way. The ore is measured or weighed in hoppers located in front of the bins, and from these hoppers the ore is spouted into the converters.

The method adopted, in recent years, for handling the slag made in the converters is to pour the slag into ladles, which are taken by the overhead cranes to the reverberatories into which the slag is poured. The reverberatory is used as a settling basin for the separation of the copper that may be contained in the slags. The conditions existing at the different plants govern, in a measure, the disposal of the slag. In some plants the converter slag is required as a flux in the blast furnaces, in which case the slag is cast into molds that are arranged on a machine—either a circular table machine, like the Walker casting machine, or a conveyor type machine.

The breaking of the ladle skulls, in all the older plants, was always a slow and laborious process. It was usually done by the crane lifting a drop weight to such a height that when it was dropped on the skull it would break it into pieces of the size necessary for convenient handling in the blast furnaces.

When the new plant for the Calumet and Arizona Mng. Co.

was designed, the engineers determined to develop some scheme that would do this work more efficiently and economically. After working on several schemes, a design was adopted in which a drop-hammer for doing the work, was located on a traveling crane. The ladle skulls are dumped on a grizzly made of cast steel or cast iron gratings with six-inch or eight-inch openings. The skull is hammered until it is broken into pieces small enough to pass through the openings. The machine is operated by electric motors and is known as the McGregor skull breaker. They are being installed in several of the modern plants, as the machine has demonstrated its practicability and its economy.

The methods of handling copper, in modern plants, have been improved by handling the metal on casting machines. Two types are used, one a round table machine of the Walker type and the other the straight-line conveyor type of machine. In nearly every case a storage or refining furnace is provided, into which the copper is poured as it comes from the converters. At the Washoe works stationary furnaces of large capacity are used, but in most cases the furnace holds about seventy-five tons, more or less, and the furnace revolves through an arc sufficient to pour the copper into the molds or receiving ladle. The furnaces are provided with burners, in order that the copper may be kept hot enough to pour; or, if the larger furnaces are used, some refining of the metal is done in this operation. The possible improvements in this department will consist in the improvement in details of the machines used and in finding a metal that will make satisfactory molds.

There is considerable power required in the operation of these modern plants. All forms of power are used—steam, oil, gas, and electric power. Power is an important factor in every department, and each department requires a great deal more than formerly. While a great deal more power is required, yet it is produced more cheaply, because it is produced from the waste heat from the furnaces or is transmitted from water-power plants located some distance away.

Costs in modern plants have been reduced in every department, with the result that lower-grade ores are being treated in every mining district, and deposits of ore that formerly were too low-grade to treat are now among the most valuable in the world.

The rapid progress and development in mining and smelting in modern times have been due to the general development in all the arts and sciences and the increase in the general intelligence of the men who are engaged in this class of work. Mechanical appliances have been perfected and adapted to the problems of handling materials in every department and new machinery invented to do work that originally took large numbers of laborers.

Nearly all large companies maintain experimental and testing departments, in charge of which are competent engineers and metallurgists, who are engaged constantly in the development of new processes and perfecting the old ones that are used in the treatment of ores and in the conservation of the values that were previously wasted.

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DISCUSSION

Mr. Ricketts.

Mr. L. D. Ricketts,* Mem. Am. Inst. M. E., spoke approvingly of the narrow water jackets, and, in this connection, commended the work of the late Charles Selby, who introduced this and many other improvements into copper smelting. He also raised the question as to proper material for copper moulds. On the whole, he considered the copper mould as at present in use to be the best, although it might be possible to develop a cast-iron mould which would give satisfactory service.

Prof. Peters.

Prof. E. D. Peters,* Mem. Am. Inst. M. E., said that there are a few men left who were smelting copper ores in the reverberatory furnace between 1870 and 1880, and it may be instructive to consider for a moment why they were unable to smelt, on an average, more than 10 to 12 tons of ore per furnace in 24 hours.

He thought that if a young reverberatory foreman of the present day could be set down suddenly in a similar plant of 45 years ago, the first and most striking impression that he would receive would be that the furnaces were not constructed to produce a sufficiently high temperature for rapid smelting.

This resulted mainly from the fact that the fuel was not burned with sufficient rapidity and regularity, and the process was not conducted in a manner to avoid the frequent admission of cold air to the hearth.

He did not think that this faulty and extravagant method of smelting arose entirely from the fact that they were ignorant of the enormous advantage to be derived from generating and maintaining a temperature in the hearth far above the actual melting point of the ore. On the contrary, he had heard this matter emphasized over and over again, at that period, at meetings of metallurgists. It was rather that the con-

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Prof. Peters.

struction and management of the furnaces were such that they could not stand a long-continued intense heat, and that the floating-up of layers of the hearth or the bursting of matte through the side-walls was pretty certain to follow any systematic attempt to maintain a large body of matte upon the hearth, or to run the furnace long at what was then considered to be an excessive temperature.

These accidents resulted almost entirely from the undercutting of the lining walls of the hearth—and especially of the bridge-wall—by the slag, and the consequent penetration of the matte into the side-walls and beneath the hearth. This undercutting of the walls was constant and serious in the majority of furnaces, demanding a careful fettling after each second or third charge, and often after every charge.

According to his own experience, this rapid cutting resulted mainly from three causes, which he named in the order of their importance:

1. The absence of a thick protecting layer of silicious ore maintained at this vulnerable point where hearth and lining walls join.
2. The unsuitable character of the fire-brick then employed.
3. The imperfect mixing of the constituents of the ore charge.

The third point is the only one requiring explanation.

The flux for the all-too-abundant silica of the charge usually consisted then, as it does now, of roasted pyrites. Reverberatories were usually charged by shoveling the material into side doors—an operation which, even when performed by four or six skilled men, cooled the furnace so seriously that at least one hour of steady firing was required to restore the temperature even to the very moderate point at which it stood at the beginning of the charging.

The various constituents of the charge were weighed in wheelbarrows and were dumped in a heap upon the charging plate below the furnace door. In the majority of cases with which he was familiar no further mixing of these separate constituents was undertaken, excepting such as resulted from shoveling the heap into the furnace.*

The consequence of this careless system of charging was that when the different constituents reached their final resting place upon the hearth, they were often segregated to a marked degree. An area of highly silicious ore might occupy one spot, while a large patch of almost pure roasted pyrite would be lying beside it. This produced extremely bad results, because the silicious area required abnormally long firing and high heating before it would liquify at all, while the iron oxide area melted with great ease and, finding itself in need of silica, naturally took up this substance from the nearest source. This source was, at times, the hearth itself; at other times, the fettling that pro-

* At the Boston & Colorado Works at Black Hawk, Colorado, great pains were always taken to mix thoroughly the various ores and fluxes before they were charged. This enabled Pearce to do rapid smelting, and to fuse a considerable number of ore-charges without tapping or fettling.

tected the side-walls; but, whichever it was, the result was disastrous to the furnace. Prof. Peters.

Propinquity is essential to the union of an acid with a base, and the more thoroughly this propinquity can be effected before the operation of smelting is begun, the more rapidly will the latter proceed.

Such an obviously shiftless way of managing a furnace will seem incredible at the present day; but, at the time to which he referred, the superintendent of the plant usually had little or no practical knowledge of smelting, was often also the mine manager, and was fortunate if he did not have to do his own assaying and chemical work. The management of the smelting operation was usually left in the hands of Welsh smelters, who, although excellent furnacemen in many particulars, were singularly unwilling to swerve at all from the practice that they had learned at home, however unsuited to American conditions these ways might be.

The conditions that he enumerated caused rapid erosion of the thin fettling. This demanded constant attention and frequent renewal at peril of serious mishap, and this meant frequent and long-continued cooling.

In 1875 he made as careful an estimate as circumstances would permit of the proportion of time during which the temperature upon the hearth (not in the space above the fire-bridge) equalled or exceeded the average smelting point of the charge. This determination embraced several European furnaces and a number of American ones, and included two under my own charge. The result indicated that an actual smelting temperature existed considerably less than one fourth of the time; thus a reverbatory of that period expended three fourths of its time and fuel in recovering lost heat and in getting ready to smelt.

The great improvement initiated by Pearce at the Boston & Colorado smelter, and later expanded by the Butte metallurgists, proved that a furnace could be constructed and protected in such a manner as to furnish great size of hearth, a solid junction independent of frequent fettling between lining and bottom, a roof and sides of silica brick capable of withstanding continuous high heat, and a permanently hot bottom uncooled by any air vault.

Under Mathewson and his able foremen the Anaconda Company pushed these improvements with great rapidity and success and, in conjunction with other metallurgists whose work must not be ignored, soon learned how to reap full advantage from the logical effects of these beneficent changes.

Prof. Peters felt that the modern practice is too familiar to all to warrant detailed mention in this brief review.

The older metallurgist had no encouragement to strive toward continuous work in the reverberatory, because the furnace simply would not stand a long-continued uninterrupted heat much above the fusion-point

Prof. Peters.

of the ore. It needed the frequent cooling periods to maintain the integrity of its structure.

When this integrity became guaranteed, there followed logically the series of improvements by which this continuous high heat was produced and maintained, namely: an uncooled hearth, the charging of hot ore, the retention of a great body of matte and slag in the furnace, the abolition of cold air from hearth and fire-box, the cleansing of grate and removal of fused products without interruption of the smelting operation, and many other advances.

There remained one fatal defect in the reverberatory process as compared with its rival—the blast furnace. It is necessary to allow the gases to escape from the hearth at a temperature not too far below the melting point of the slag. This enormous waste of heat has been obviated by employing these waste gases for the generation of steam, and 30 to 50 percent of the original calorific value of the fuel is now utilized in this manner. The employment of pulverized coal as fuel is the latest radical improvement in this type of smelting, and its economy has been demonstrated beyond all doubt.

It is obvious that, without modern appliances and methods, it would be impossible to convey and remove the enormous amount of ore and melted products that belong with the furnace practice of today.

Speaking roughly, we smelt today 500-ton charges per 24 hours on a reverberatory hearth having an effective area of 1800 square feet. This is at the rate of 555 pounds per square foot. In 1874 Prof. Peters thought he was doing remarkably well when he smelted 12 tons per day on a hearth area of 112 square feet, or 215 pounds per square foot.

In 1874, it required about one man-shift to four tons of ore smelted; at present, he believes that at least 25 tons per man-shift is reached.

His thesis is that it is improvement in the construction of the furnace that has made these results possible.

Paper No. 177

LEACHING COPPER ORES.

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INTRODUCTION.

Hydrometallurgical methods of extracting copper and associated precious metals from ore have received material impetus during the past few years through experimental work carried out under the auspices of large American copper companies. The more progressive of these corporations, realizing benefits to be derived from free discussion of the problems involved, have permitted detail accounts of their operations to be given out, and a number of articles broadly covering the field have recently appeared in technical publications.

A list of the companies which have been investigating adaptability of leaching methods to their ore, and intermediate products, would include practically all the large operating copper companies in this country, and many smaller ones, and net results have been that several large copper-leaching plants are in course of construction, while some are already in operation.

This paper has been prepared with the object of correlating some of the important data obtained through recent experimentation, and of indicating sources from which additional details may be had. Space does not permit describing, or even mentioning, all the leaching processes proposed or still in the experimental stage.

It is a well recognized fact that the treatment of ore at each mine, or in each mining district, presents a problem in itself. Furthermore, the ores from different mines, even in the same district, often disclose individualities which require modifica-

tion of the treatment accorded them. There are few metallurgical processes which are applicable without alterations to all ore, even when it is of the same general class. Until local conditions have been studied it is impossible to say which method, or combination of methods, of recovery will prove to be most economical in a given case. A process which has been found satisfactory in one locality may not be adaptable in another until essentially altered to meet new conditions. An apparently unimportant difference in composition of an ore, or in local economic conditions, may vitally influence the outcome. The matter of ore-treatment, at any mine, should be approached without predilection for any particular method of reduction, and the factors which enter into the problem should all be carefully weighed, if a decision is to be reached that will be fair to the particular case under consideration.

Acquiring knowledge through experimentation is usually expensive, and the great importance, to mining interests in general, of the free distribution of valuable data by American mining companies is apparent. The metallurgical information made available in this way, supplemented by that supplied from the research laboratories of Europe, has reduced necessity for long and costly experimentation on part of those seeking information as to ore-treatment in specific cases. It is now possible to avoid useless duplication of experiments, and to reach conclusions promptly without incurring heavy expense.

Much data of value, unfortunately often embryonic, can also be culled from patent specifications. It is instructive to learn what has been attempted, even if the hopes of sanguine projectors of numerous schemes were not realized. At the present day there is rarely any excuse for the costly metallurgical failures which formerly characterized application of the art, and where such occur, the cause is usually due to disregard of well-established facts.

Leaching is not a panacea for the woes of the mine owner who has ore that assays well but which he has learned through experience cannot be handled profitably by methods of reduction which may have been tried. If such an ore cannot be shipped to some metallurgical center and made to yield something above the expense entailed in taking it out and shipping

it, and if familiar methods of ore-treatment have been found disappointing, it may be sometimes of advantage to investigate possibilities with regard to leaching it. Leaching methods have in some instances solved the problem of extracting valuable metals from immense quantities of material which until recently lay unproductive. As illustrating this point the case at Chuquicamata (Chile) may be cited, where 200,000,000 tons* of ore have been developed, assaying about two percent copper, for handling which a leaching plant of 10,000 tons daily capacity is nearing completion. The existence of this ore-body has long been known; but antecedent to experimentation with leaching methods, all attempts at profitable exploitation of these deposits proved unavailing, as shown by the fact that this great body of ore has remained practically untouched for many years.

Another instance of intelligent application of leaching methods to ore reduction is found at Anaconda, where mill-sand assaying on the average 0.6 percent copper, and half an ounce silver per ton, has finally been successfully treated by lixiviation. The first unit (2000 tons daily capacity) of a large leaching plant is under construction at this point.

The Calumet & Hecla Company of Michigan is building a 4000-ton leaching plant to treat tailing carrying about 0.5 percent copper.

There are many others experimenting, building, or operating, so that the outlook appears very encouraging for the application of leaching methods to extraction of copper and intermediate products from suitable ore.

In investigating adaptability of lixiviation to any particular ore, it is necessary to examine carefully into character of ore, water supply, cost of power and fuel, and of substances available as lixiviants and precipitating agents, to ascertain whether or not leaching is at all practicable in the premises. Some common errors may be considered as not calling for experimental investigation, among which might be mentioned the use of acid lixiviants with ore carrying large quantities of calcium carbonate, and employment of electric current for deposition of copper from solutions the nature of which is manifestly unsuitable for elec-

* The ton used in this paper refers to the short ton of 2000 lb. (= 907.2 kilograms)

trolysis or in localities where power is expensive. The appearance of calcium oxide in the general analysis of an ore is of itself not a determining factor; for that base may be so combined as not to be attacked by the lixiviant employed.

Any ore may be leached with the help of chemicals in a laboratory; still, for several reasons the method employed experimentally may not be practical in the field. The cost of necessary chemicals may be prohibitive, or suitable apparatus in which to carry out required operations may be unattainable, or the proposed process may be so complicated as to preclude possibility of financial success from the start, etc. As in most cases of prospective leaching, only low-grade ore comes under investigation; two features essential to success should never be lost sight of: the process must be made as simple as possible, and a sufficient quantity of material must be handled daily to permit of a profit which will adequately cover all expense entailed in its treatment. Due regard for simplicity of operation, and tonnage, are prime factors in successful leaching operations.

ORE SUITABLE FOR LEACHING.

With regard to the amenability of copper ore to leaching methods, the field is not a restricted one. Mr. Stuart Croasdale* has shown what can be done with the porphyritic ore of the Southwest carrying 1.45 percent copper and negligible quantities of the precious metals. When crushed to pass 2-mesh screen, an acid lixiviant extracted about 78 percent of the copper from this ore. An analysis of the ore treated is given by Mr. Croasdale, as follows:

Analysis of Leaching Ore from Ajo.

SiO_2	63.29%
Fe	4.20 "
Al_2O_3	14.30 "
CaO (soluble in acid)	0.90 "

* "Leaching Experiments on the Ajo Ores", Transactions of the American Institute of Mining Engineers, Salt Lake meeting, August, 1914. All data referring to Ajo contained in the following pages are derived from Mr. Croasdale's paper.

MgO	0.80%
MnO	0.14 "
S (total)	0.27 "
S (as sulphate)	0.10 "
Cu (total)	1.45 "
Cu (soluble in 10% H_2SO_4)	1.32 "
CO_2	1.26 "
Au	0.01 oz.
Ag	0.18 oz.

At the leaching plant of the Butte-Duluth Mining Co. a "decomposed granite" carrying copper silicates and carbonates, with some cuprite (total copper about two percent), is being leached on a commercial scale. Incidentally it might be mentioned that in leaching crude cupriferous ore containing cuprite, using dilute sulphuric acid solution, only half of the copper can be extracted from the cuprite, because, under such conditions, Cu_2O falls into CuO and Cu, and metallic copper is not attacked by dilute sulphuric acid. However, this mineral is dissolved by ferric salts, and as these are usually formed when iron is present in an ore, the copper may be recovered in this way.

Throughout the Western States, and Mexico, there are a number of garnetiferous copper-ore deposits. Often the copper in these is oxidized to some extent, and the heavy garnet gangue makes them difficult to treat by mechanical concentration. Such material, assaying about two percent copper and carrying considerable calcium oxide, may be readily percolated with sulphuric acid solutions, and an extraction effected of over seventy percent of the copper content when reduced to 4-mesh. If ground to 16-mesh and agitated, eighty odd percent can be easily attained.

Mention was made above of the mill-sand successfully lixiviated at Anaconda. An analysis of this tailing is given by Mr. Frederick Laist.*

* "Roasting and Leaching Tailings at Anaconda, Mont.", Transactions of the American Institute of Mining Engineers, Vol. XLVI, page 375. Wherever reference is made to Anaconda in the following pages the data have been obtained from the above mentioned paper, or from the papers presented at the Salt Lake meeting of the Institute in August, 1914, by Messrs. Laist, Frick and Aldrich.

Analysis of the Tailing Treated at Anaconda.

Cu	0.6%
SiO_2	82.2 "
Fe	1.9 "
S	2.2 "
Al_2O_3	9.4 "
CaO	0.6 "
	96.9%
Ag	0.55 oz.
Au	0.002 oz.
Moisture about	5%

Successful treatment of the cupriferous granodiorite of Chile has also been referred to, and will be enlarged upon further down.

The most desirable ore to lixiviate is one containing copper mineralized as carbonate, with a silicious gangue. Where copper is mineralized as sulphide it can be oxidized by roasting, unless cost of fuel is prohibitive; and for leaching purposes, roasted material presents advantages over crude ore in most instances.

The suitability of leaching methods for copper mineralized as silicate has been the subject of some controversy. The cause of differences of opinion on this head is probably due to confusion as to what constitutes silicate of copper (chrysocolla). Much green copper-mineral exists which is too complex for accurate mineralogical identification and yet carries the metal combined with silica. Sometimes the mineral appears to be a mixture of different combinations of copper and silica, which vary in color from pale green into many shades of blue. Again copper silicates are found mixed with the carbonates, such ore being referred to in common parlance as "carbonates". Copper silicate is stated, by some, to be practically insoluble in dilute sulphuric acid, even a ten percent acid solution is said to have little effect upon it. Others report trouble in leaching copper silicate ore owing to formation of gelatinous silica, and soluble silica is said to have interfered with the deposition of electrolytic copper through precipitation on the electrodes. Evidently different combinations of copper and silica were subjected to investigation by the respective observers. Green stains on or through

silicious material such as sandstone, or other absorbent or porous forms of silica, have been found to contain no carbonic acid, and produced no soluble silica such as would interfere with electrolysis. In one case such an ore, which carried fourteen per cent copper, though neither carbonate nor sulphate was in evidence, was readily leached by either hydrochloric or sulphuric acids without formation of soluble silica. Such material is, of course, very suitable for leaching.

Probably much of the greenish-blue ore which occurs so profusely in the upper portions of copper mines is the basic sulphate of copper (brochantite). Lindgren* writes: "It is believed that a careful examination of many so-called malachites from other districts will disclose the overlooked importance of brochantite as a copper ore. * * * On the whole the mineral is most abundant in fissure veins in porphyry, though also occurring in the irregular deposits in limestone". Mr. Lindgren was writing of the Clifton District (Arizona). At Chuquicamata, brochantite is the principal copper mineralization.

It is not surprising, therefore, that variance of opinion should exist with regard to the leaching qualities of the greenish-blue copper ore-bodies of such diverse mineralization. The ore being leached at the Butte-Duluth Copper Company's plant is said† to contain copper mineralized as silicate as its principal copper constituent, and no difficulty is found in dissolving out eighty odd percent of that metal. Also the silicate of copper leached at the Steptoe works (Nevada)‡ is readily soluble in sulphuric acid lixiviant. After a study of the data available from a number of sources relative to the leaching qualities of copper silicates, it becomes apparent that combinations of copper and silica exist which have proven resistant to some extent to the action of sulphuric acid under the conditions of its application; but for the most part, such combinations may be easily decomposed by suitable lixiviants.

* Professional Paper No. 43, page 119, U. S. Geological Survey.

† C. S. Herzig in Bulletin of the Institute of Mining and Metallurgy, May, 1914.

‡ Transactions of the American Institute of Mining Engineers, Salt Lake meeting, 1914.

CHOICE OF LIXIVIANTS.

Many lixiviants have been proposed for leaching copper ore, and these have been tested—at least in laboratories. However, the choice of the operating companies seems to have narrowed down to the use of sulphuric acid, wherever calcium carbonate does not interfere. This apparent restriction in the selection of a lixiviant may be reconsidered when more experience has been gained. A strong acid solvent acts not only on the copper, but also carries a number of other elements into the solutions, with attendant disadvantages. It would seem more to the purpose, when character of the ore permits, to employ reagents which exercise a selective action.

At Anaconda, where the mill-sand is roasted, salt (NaCl) is added to the lixiviant for extracting silver, and to improve recovery of copper; but even there sulphuric acid is the basis of the solvent solution.

Lixiviants containing chlorine in different forms have been repeatedly tried, but they have never proved satisfactory. The Hoepfner process is probably the best known of the chlorine methods. It has been tested at several places on a working scale, but subsequently abandoned. It has been often described in the technical press.

Another attractive chlorine process was developed by Froelich,* but it also seems to have met with no commercial success. Many other processes based on the solvent power of chlorine, free or combined with other elements, have from time to time appeared; but as far as known none have been adopted commercially. Mr. John D. Fields who has been connected with several copper-leaching operations, writes:† "It may be accepted as a foregone conclusion that the failure of all processes, designed to precipitate electrolytically, that involve chlorine as a factor in the leaching of ores containing considerable amounts of alumina, soda or potash, or the introduction of sodium into the pulp during the process of treatment, no matter how interesting they are from an experimental standpoint, is sure".

As sulphuric acid enters so largely as a factor into leaching

*"Metallurgie", 1908, pp. 206-209.

† Engineering and Mining Journal, Jan. 3, 1914, page 32.

operations in the present state of the art, the cost of this commodity is of interest when making an estimate of the probable expense of treating a given ore. It is important that all reference to acid consumed or used in lixiviation should be made in terms of H_2SO_4 and not of commercial acid, because there are several grades of acid on the market, and confusion arises from this source as to the precise quantity of actual H_2SO_4 used per pound copper produced. Roughly speaking, it will require fifty percent more 53° B. acid to produce the same results as when 66° acid is used, and 25 percent more 60° acid.

In the vicinity of smelting works sulphuric acid can probably be had at moderate cost—$3.00 has been mentioned as the estimated expense of producing it at Anaconda. At the Butte-Duluth plant it was estimated that acid could be manufactured on the ground for $4.00 per ton, but at the time of the writer's visit to those works the acid used was costing $27.00 per ton delivered at the mill.

At Clifton (Arizona), where leaching copper has been carried on for a number of years, and where the company has its own acid chambers and mines its own ore, the acid is said to cost about $10.00 per ton. A small leaching plant near Luning (Nevada), situated four miles from a railroad, had to pay $33.00 per ton for its acid.

It is not necessary to purchase high-grade commercial acid for leaching purposes when sulphide ore is attainable in the vicinity of the leaching plant, because there are several ways of condensing roaster gases and of converting the sulphur dioxide contained in them into an acid liquor sufficiently strong to be used in extracting copper from its ore.

LIXIVIATION COMPARED WITH OTHER METHODS OF ORE REDUCTION.

Croasdale has shown that the porphyritic copper-ore of the Southwest, notably the semi-oxidized material found at or near the surface, may be successfully leached with sulphuric acid lixiviant when crushed to 2-mesh and treated in the raw state. The average extraction was not high (78%), and bringing the metal out of solution into commercial form will, of course,

occasion further loss—ten percent will be probably an outside figure—yet it must be considered that the ore was crushed to 2-mesh only, and that the tests indicate that crushing to 0.75 inch might answer equally well. It was thought that as good extraction could be made from the sulphide ore of the same mine, as from the oxidized, by giving it a preliminary roast. It is reasonable to expect, as experience is gained in handling this ore by the method indicated, that the percentage of extraction will be increased.

Similar ore is now being treated in several other districts by a combination process comprising mechanical concentration and smelting, supplemented by electrolytic refining. It is interesting to compare the recoveries effected by this method of reduction with the data obtained at Ajo from leaching tests.

Mr. Heath Steele* has compiled an instructive statement as to the actual percentage of recovery made from porphyry ore by some of the largest operating companies. The following are Mr. Steele's figures:

		Percent actual Recovery
Utah Copper	1910	55.6
" "	1911	59.9
" "	1912	57.4
Miami Copper Co.	1911	66.7
" " "	1912	61.0
Ray Consolidated	1911	50.6
" "	1912	51.2
Nevada Consolidated	1910	70.0
" "	1911	69.5
" "	1912	66.0
Chino Copper Co.	1912	55.0

As the annual tonnage treated by the corporations enumerated above runs into many millions, the inefficiency of the methods of reduction employed represents an enormous waste of national resources, for subsequent recovery of the copper run out of the mills in the tailing is very improbable. Referring to the inadequate methods at present employed in reducing porphyritic copper ore, Dr. Rudolf Gahl† writes: "The concen-

* Mining and Scientific Press, June 7th, 1913, page 865.

† Transactions of the American Electrochemical Society, New York meeting, April, 1914.

tration process has been developed to such a state of perfection that on clean sulphide ores recoveries of 85 percent of the copper can be obtained. Unfortunately the ores that generally are called porphyry copper ores are not of this character, as they contain a considerable percentage of their copper in the oxidized state. . . . The water concentration process is, up to the present time, not able to extract copper in oxide combination with an efficiency approximating the extraction of the sulphide copper. I believe that 30 percent is an average round figure for the extraction effected on the oxidized portion of the copper in sulphide ores. It follows, that where ores are largely contaminated with such material, no satisfactory saving can be obtained by ordinary concentration methods. A great many of the mines in Arizona and New Mexico suffer under this disadvantage (Chino, Shannon, etc.)".

Among the many schemes for ore-treatment which have made their reappearance in recent times, most of which are not novelties, is the flotation process. This treatment when applied to oxidized copper ore gives practically negligible results—as far as reported.

The operations comprised in leaching ore are the following:

Bringing copper into solution.
Separation of pulp from lixivium.
Recovering copper from solution.
Treatment of the deposited copper products.

This sequence will be followed in the succeeding pages.

CRUSHING THE ORE.

As practically all copper minerals found in oxidized surface ore are secondary products, they frequently lie along fracture planes, and it is often only necessary to crush such ore so that it falls to pieces along such lines of weakness in order to expose the copper minerals to the action of solvent in the leaching vats. In the case of the Ajo (Arizona) porphyry, Croasdale found that crushing to 4-mesh was all that was necessary to effect an extraction of 78 percent, and was led to the conclusion that even coarser crushing might have answered as well. A screen analysis of the Ajo crushed ore is given as follows:

Screen Analysis of Ajo Crushed Ore.

+ 4	19%
+ 8	25 "
+16	18 "
—16	38 "
	100%

At the Bullwhacker (Montana) leaching plant the ore was crushed to pass 16-mesh, and an extraction of over 90 percent was said to have been secured from the crude ore. Formerly the Butte-Duluth (Montana) ore was crushed to 2-mesh and percolated raw in V-shaped vats, with a reported extraction of about 80 percent; but recently a change was made and the ore is now crushed to about 10-mesh with a reported extraction of 92 percent.*

The following screen analysis of the mill-sand leached at Anaconda (Montana) shows that a high extraction can be made from a comparatively fine material by percolation.

Screen Analysis of Anaconda Mill-sand.

+ 14	4.50%
+ 40	50.31 "
+ 60	15.33 "
+ 90	11.45 "
+110	6.54 "
+160	5.52 "
+200	2.86 "
—200	5.31 "
	101.82%

In some experimental work undertaken by the writer on garnetiferous surface ore, carrying much of its copper as silicate, it was found that an extraction of 70 odd percent of the copper could be relied upon when the material was crushed to about 4-mesh. In general, it may be said that fine crushing of copper ore, when it is to be subjected to leaching, is to be avoided where possible, because slime interferes greatly in several ways. When the mineral is dense, and not readily penetrated by the solvent,

* Engineering and Mining Journal, August 1, 1914, page 220.

a slight roast often renders it porous, even when comparatively coarse—through removal of moisture and chemically combined water, disengagement of carbonic acid, and alteration of the contained sulphides.

ROASTING.

At the Intercolonial Copper Company's plant (Nova Scotia) the ore is roasted to sulphatize the lime and oxidize iron sulphide to ferric oxide.* The hot ore is allowed to fall into a solution containing five percent sulphuric acid.

It has been found beneficial to roast an ore sometimes, even if no sulphide minerals are present, for in this manner the iron and alumina content is rendered more or less insoluble, and the adsorption of copper by colloids is avoided. Adsorption is the property possessed by certain clays, and other material, of extracting metals from dilute solutions. Lindgren found that crushed clay from Morenci (Arizona) extracted 90 percent of the copper from certain solutions.

Roasting an ore with the object of improving its leaching qualities is a very different matter from roasting with subsequent smelting in view. Expensive failures have occurred through neglect of proper precautions in roasting preparatory to lixiviation. The type of furnace used must be adapted to the change which it is desired to produce in the ore. With modern mechanical furnaces the expense of roasting is small, the metal in copper sulphides and cuprite is rendered soluble, and deleterious elements are kept out of the electrolyte, which is thereby made suitable for electrolysis.

Two methods of roasting are practiced in preparing copper ore for leaching: oxychloride roasting, and plain oxidation. The choice of one or other of these is influenced by the presence of silver in an ore in sufficient quantity to warrant extraction. Some difference of opinion exists with regard to benefits accruing from applying the two methods, a purely oxidizing roast being thought by some to have several advantages over chloridizing. In favor of the oxidizing roast, it is claimed that valuable metals are

* R. R. Goodrich in Bulletin of the American Electrochemical Society, New York meeting, April, 1914.

volatilized to a lesser extent; accretions in the furnace are avoided; extraction of copper from the pulp is better; but it is admitted that silver recovery is not as good. On the other hand, the addition of salt (NaCl), even when carrying out a sulphatizing roast, has been found to produce beneficial results.

Laist and Aldrich* have given following details of tests made on a large scale at Anaconda, using a chloridizing roast. The feed carried 0.6 percent copper and 0.55 oz. silver. Copper extraction was 78.9 percent. All volatilized metals of value were assumed to be recoverable. The same authorities state that further tests showed no salt was necessary in achieving a roast suitable for the extraction of the copper alone, but that salt did increase the silver extraction from 75 percent to 90 percent. This extra 15 percent recovered would, however, not pay for the increased cost of the salt used and installation and operation of apparatus necessary to effect condensation of the volatilized metals. Scrubbing towers did not work well in condensing the fume from oxychloride roasting and a Cottrell electrical precipitation unit was tried. With the help of this apparatus 90 percent of the copper, and a considerable amount of acid, were recovered from the fumes. However, it was found preferable to chloridize the silver subsequently in the leaching vats.

When tests were carried out on practically the same material, and no salt was added to the charge in the roasting furnace, the results were as follows: assay of feed (calcine), 0.68 percent copper and 0.57 oz. silver; extraction, 84.4 percent of the copper and 70.9 percent of the silver. An investigation was made of the percentage of extraction effected in the upper and lower parts of the leaching vat, respectively. It was found that copper extraction in the upper half was 86.2 percent, and in the lower 82.8 percent.

The roasting furnace used in the 80-ton experimental plant at Anaconda was a six-hearth McDougall, twenty feet in diameter. There were two fire-boxes placed on opposite sides, the flames entering on the third hearth. A Buffalo blower, working as an exhaust, produced the draft. When operating under standard conditions of temperature and pressure, between 3,500,000

* Transactions of the American Institute of Mining Engineers, Salt Lake meeting, August, 1914.

and 4,000,000 cubic feet of gas were drawn out of the furnace in 24 hours. The temperature of the outgoing gases was about 180° C. Air was used for cooling, and 850,000 cubic feet were forced in under 15 lb. pressure.

In roasting copper ore for leaching, the temperature of the furnace must be under perfect control to produce the uniform product so essential in succeeding operations. For this reason the same grade of fuel should be maintained, and sulphur content of the charge should not vary greatly. The temperature should not be permitted to sink below 880° F. (471° C.) on the fourth hearth. Should the temperature on this hearth fall below that indicated, it is difficult to get it back again.

The best temperature for roasting Anaconda mill-sand was found to lie between 900° (482° C.) and 930° F. (499° C.). At, or above, 1000° F. (538° C.) ferrites formed. The percentage of moisture in the feed seriously affected operation of the furnace. The average moisture was five percent: when it reached eight or ten percent the charge banked over the arms and interrupted operation. Ninety tons of mill-sand, containing five percent moisture, 0.68 percent copper, and a proportional amount of sulphur, can be roasted in a twenty-foot McDougall in 24 hours, with coal consumption amounting to 2.75 percent of the dry weight of the charge. A feed containing three percent of sulphur is reduced to 0.6 percent, and forty percent of the copper in the calcine is rendered water-soluble.

The most efficient cooling device for the pulp discharge from the roaster was a rotating drum made of quarter-inch boiler-iron plate. This drum was water cooled. When the furnace was treating eighty tons of material, 25,710 gallons water were required for cooling purposes in 24 hours. The temperature of the calcine was reduced in this manner from 260°—370° to 45° C. A screw conveyor transported the calcine from the cooler to the leaching vats.

There are several furnaces besides the McDougall, all of the same general type, which may be employed for roasting preliminary to leaching. Prominent among these are the Wedge, and the Herreshoff (Manufactured by the Pacific Foundry Co. of San Francisco). They have large capacity and operate

cheaply. In the admirable work on unit construction costs* by E. Horton Jones, the complete cost is given of a Herreshoff roasting-furnace plant set up at Clifton (Arizona). These roasting furnaces had six superimposed hearths and a top drying hearth. The outside diameter of the shell was 21 feet 7¼ in., and the arms were air-cooled. The cost given includes the roasters and roaster-buildings, roaster dust-chambers, and roaster dust-chamber flue. The total cost per roaster was $24,907.34.

There are other types of roasting furnaces which are less expensive than those referred to above, and which have proven satisfactory in preparing copper ore for leaching. In selecting a roasting furnace to perform certain work, the character of the ore, the temperature necessary to produce the desired changes, and the condition of the calcine best adapted to the purpose in view, all have to be given consideration. Usually perfect control of the air admitted to the furnace is very essential. The success of a leaching plant may depend upon the roaster.

PERCOLATION AND AGITATION COMPARED.

Percolation may be defined as the treatment of stationary pulp by moving solutions: in agitation, both the pulp and the liquors are kept in motion. Both systems present advantages. Coarser material can be handled by percolation than by agitation, but more time is required to bring the metals into solution. In percolating the porphyritic ore of Ajo, Croasdale reached the conclusion that in crushing the ore so that it would pass through a screen with ¾-in. apertures it would be reduced small enough to permit good extraction. It was found that crushing to 4-mesh seriously interfered with percolation, and resulted in loss of time and low extraction. When the ore was crushed to 2-mesh, the leaching was very uniform, and channeling was avoided. Crushing to 4-mesh resulted in segregation of colloidal slimes, and the leaching was not so uniform. The colloidal slime, which amounted to five percent, was apparently not due to action of the lixiviant. In percolating ore containing soluble iron, alumina, or calcium combinations, insoluble salts of these elements are apt to form in

* Transactions of the American Institute of Mining Engineers, Salt Lake meeting, 1914.

portions of the charge where the acid content of the lixiviant has been weakened, causing irregularities.

In charging leaching vats care must be taken to avoid segregation of particles of crushed material in the act of placing the ore. If dry ore is thrown into a tube several feet in height, it will be noticed that the particles separate in layers, the coarser being at the bottom. If the tube is previously filled with lixiviant and the ore is then charged, this phenomenon is intensified, and a five-foot column of ore crushed to 4-mesh can become impermeable to solutions. This difficulty may be overcome by dampening the charge in advance of placing it in the vat, causing the fine particles to adhere to the coarser. The charge must not be wet, or it will pack.

The practical limit in height of ore-columns which will permit rapid percolation has not been definitely determined. At Anaconda the mill-sand (screen analysis of which is given in a previous section) was percolated in a ten-foot column. At Chuquicamata the leaching vats are being built sixteen feet high. At Ajo an eighteen-foot ore-column was tried, with very little diminution in the rate of percolation. In practice the height of ore-columns to be leached will be determined more by convenience in removing the leached material from the vats, than by other features.

Percolation may be upward or downward. If carried out in an upward direction the lixiviant spreads gradually throughout the whole vat, displaces air, and tends to keep the fine material in a state of suspension. The use of a filter is unnecessary. If percolation is downward, there is a tendency to drain the charge through channels, and the fines are carried down and deposited on the filter. Simplicity of construction should be one of the main objectives sought in designing apparatus to handle low-grade ore in bulk, and gravity filters and filter-presses should be avoided where possible. Croasdale recommends passing the leach-liquors in at the bottom of the vat at first to displace air, and after the ore is covered, to reverse the current and percolate downward. It is claimed that this method gives better control of solution, and permits use of minimum quantity of wash-water later on. It is also stated that by keeping the ore covered with solution, and maintaining the circulating capacity a little above

rate of percolation, channeling may be detected and regulated. An alternate method suggested is to admit the lixiviant on top of the dry ore, but at one side of the vat, whereby the liquor passes at once to the bottom and collects, expelling the air as it rises. It was found unadvisable to saturate the ore with water before applying the lixiviant, because in that case water has to be displaced by acid solution before the mineral is acted upon, which delays the operation and serves no useful purpose.

At Anaconda a method of repeated draining and resaturating the pulp appears to have given satisfaction. When a charge is drained and again flooded, all particles are presumed to be reached by fresh acid solution. In one of the most satisfactory tests made at Anaconda, calcined sand assaying 0.713 percent copper was given a six-day treatment. A strongly acid solution was first put on the charge, and drained. Then a second portion of lixiviant was added to resaturate the pulp, and this portion was brought up to fifteen percent acid for the solution traveling down through the charge. Repeated draining and flooding seemed to help extraction. After the charge was sufficiently drained, and before wash-water was added, salt (NaCl) amounting to one percent of the weight of the charge was spread over the top. The strong saline liquor formed upon addition of wash-water, in passing downward through the charge washed out the remaining chloride of silver. By sending back to the solution tanks the first salt liquor drawn off to replace discarded solution, very little salt was lost in the wash-water.

Percolating the charge, draining, and then passing air through the moist pulp, was also tried at Anaconda, but with doubtful benefit—it also prolonged the cycle of operations. Repeated draining and resaturating were thought to give better results than forcing in air. Sprinkling the ore with solution was also tried instead of flooding it. The results did not indicate any advantage over flooding, and complicated operations by introduction of automatic sprinklers. The flooding system was thought to offer fewer difficulties, and, if anything, to do better work.

In leaching, the quantity of solution absorbed by the ore is a matter of importance, because of intimate connection with loss of salts in the tailing. At Ajo, porphyry ore crushed to 4-mesh absorbed eleven percent of its weight of water, amounting to

26.4 gal. per ton: crushed to 2-mesh, it absorbed six percent of its weight, or 14.4 gal. per ton of ore. Fifteen percent additional water, amounting to 36 gal. per ton, was required to fill interstices and cover ore in a vat. The average amount of solution needed to cover one ton of ore after saturation was 34 gal. At Anaconda the weight of solution necessary to saturate a charge was found to be twenty percent of the weight of the calcine, assuming specific gravity of solution to be one (in reality it was about 1.25). It required from six to seven hours to drain off a vat containing ten feet of mill-sand so that the moisture held back should not exceed ten percent.

Croasdale furnishes some interesting data as to the rate of percolation through porphyry ore at Ajo. With an ore-column twelve feet in height and ten inches in diameter, circulating the solution from the bottom, one gallon passed in thirty seconds; at the end of 96 hours the rate was one gallon in 35 seconds. This was with ore which had been crushed to 2-mesh. Increasing the height of a dry ore-column ten inches in diameter progressively from five feet to 7.5 ft., and then to ten feet, did not diminish the rate of percolation, the flow continuing at one gallon in fifteen minutes on ore crushed to 4-mesh. At the end of 72 hours the rate was one gallon in 23 minutes, after which it gradually fell off. Another experiment made on a dry ore-column eighteen feet high, of same diameter (ten inches) as in preceding tests, gave a rate of one gallon in eight minutes. This was also on 4-mesh material, and the water was circulated from bottom to top by means of a centrifugal pump. At the end of 72 hours the flow was still one gallon in eight minutes. Further data on this interesting subject will be found in the original paper.

At Ajo the average rate of percolation per square foot of filter area in vat-leaching was found to be ten gal. per hour. The rate of percolation on 4-mesh material was only one quarter of that on 2-mesh. The effect produced by kaolinization of the ore was shown by the fact that rate of percolation through hard ore was twice that through the softer 2-mesh material, and eight times that of kaolinized ore crushed to four mesh.

Agitating pulp with lixiviants naturally brings about improved extraction and great saving in time, because fresh lixiviant is constantly forced into contact with particles of ore;

but for this purpose, the pulp must be quite fine in order that it can be held in suspension. Fine crushing in copper leaching has its disadvantages, but when pulp is agitated the protection afforded the mineral surfaces through formation of insoluble salts is done away with—the said salts being removed by friction. Also, because the material treated is necessarily in a finer state of division, therefore greater surface is exposed to action of the solvent. Ore through which lixiviant has been circulated for three or four days to get seventy percent extraction, when crushed to 4-mesh, has been found to yield 85 per cent of the copper when crushed to 16-mesh and agitated by means of compressed air. Air agitation is not practicable with heavy gangue, such as garnet, when using reasonably high pulp columns.

A form of air agitation was tried at Anaconda, but did not give satisfaction. In these tests a lead pipe 1½ inches in diameter was introduced into one of the solution vats and provided with a bend at the bottom. The idea was to pass air through this pipe and so produce a swirling action in the pulp. It was found that when air under ninety pounds pressure was sent through the pipe no swirling action was produced. The air came to top of charge above where it entered and only agitated a small part of the liquor. In some tests carried out at another place, using compressed air introduced through a coil of perforated lead pipe in the bottom of a small vat, a low column of thin pulp was thoroughly agitated, but the capacity of such apparatus is not sufficient in handling low-grade ore on a commercial scale.

Circulating lixiviants by pumping is, in a sense, a form of agitation, as the liquor is forced through the ore more rapidly than it would be were gravity alone relied upon. At the leaching works of the Arizona Copper Company (Clifton), tailing ranging from pieces one inch in size down to sand (75 percent larger than ⅛ inch) was treated in large circular wooden vats with perforated false bottoms. A centrifugal pump was provided for each vat, for circulating the liquor from bottom to top of the vat.

Agitation by means of mechanically-driven stirring arms has often been resorted to, but such apparatus is of necessity of small capacity; and when from any cause the operation is arrested, the pulp packs around the stirrers and must be shoveled out.

Quite recently Dorr* has introduced a modification of his classifier into copper leaching practice.

The machine is reported to be giving satisfaction at the leaching works of the Butte-Duluth Mining Co. (Montana). Mr. C. S. Herzig† has described the Dorr apparatus as used at this plant. The original installation consisted of five machines, each 4½ ft. wide and 15 ft. long, placed in series. The first three machines were used for acid leaching; in the last two the leached ore was washed. Slime is disengaged from the sand in the first machine and kept separate. Later two machines thirty feet in length were added to the series, which gave the ore 135 feet of raking over before it went to the tailing dump. It is stated to be the intention of the management to substitute the longer machines in place of the 15-foot apparatus now in use.

The function of the Dorr machine is to rake the pulp through an inclined trough and then to push it over the end into another similar machine, where the same operation is repeated. The ore and lixiviant are first brought together in a mixer, and thence passed into the first Dorr. The pulp is supposed to leave the first machine carrying only 25 percent moisture. In the second machine the partially leached pulp is given a second treatment, this time with ten percent solution (66° B acid), the overflowing lixivium going to a storage tank. In this manner the pulp is pushed through the several succeeding machines until a sufficient extraction has been effected. Wash-water is introduced into the penultimate machine and the overflow goes back to the mixer, where it meets dry ore and is returned to the cycle. Wash-water from the last machine is passed over scrap-iron. It is expected to give the slime which overflows from the first machine a separate treatment.

The Dorr machine appears to have a future in its application to the leaching of copper ore. Its capacity is large for the floor space occupied. Agitation of the pulp is thorough, and, in consequence, extraction of copper is rapid. The power used is reported to be small; repairs are said to be light; the apparatus does not have to be dug out in case of unexpected interruptions;

*"The Dorr Hydrometallurgical Apparatus", Trans. American Inst. of Mining Engineers, Salt Lake meeting, August, 1914.

† Loc. cit.

and the process can be closely watched and is at all times under control.

STRENGTH OF LIXIVIANT.

The prevailing custom in copper ore-leaching is to employ strong lixiviants; and in this connection the relative speeds with which the several minerals are acted upon are of importance. Caspari and Flegel* state, that if the celerity with which $CaCO_3$ is dissolved by an acid is indicated by 1, then in the case of $CuCO_3$ it is 0.231. If, therefore, an acid lixiviant dissolves copper mineralized as carbonate four times as rapidly as it takes up lime from calcite, then it would be expected by rapid treatment with comparatively weak solution that copper could be leached from carbonate ore with small acid consumption.

Most oxidized copper ore shows varying degrees of alkalinity due to soluble bases present. If an acid cupriferous lixiviant is passed upward through a column of such ore, the first solution appearing at the top is often discolored—that is, the first lixivium obtained contains less copper than was in the original lixiviant. Consequently, in percolating, conditions are sometimes favorable to precipitation of copper from lixivium by alkaline substances contained in the ore. This phenomenon is more likely to be observed with percolation treatment than with agitation, because in percolation the solutions are left in contact with these agents for a longer time than when pulp is agitated.

The importance of rapidity of treatment in its effect upon acid consumption has been repeatedly noted. Mr. Claude Vautin writes: "If one had to deal with an ore where the consumption of acid was considerable, the more rapidly the copper carbonate was dissolved the lower, frequently, was the amount of acid required. In one case with ordinary percolation 40 to 60 hours were required to dissolve the copper with a consumption of from 2.5 to 3 lb. of acid per pound of copper extracted; when the same ore was more finely crushed and solution effected by agitation, the acid consumption was decreased to 60 percent (or under) of the former amount".

Croasdale found in the Ajo experiments that a 5.6-percent acid lixiviant little more than sufficed to destroy alkalinity of

* "Metal und Erz", February 8, 1913, page 254.

the ore, and but a small quantity of copper was dissolved. In these tests, however, leaching was done by percolation (24 hours), and time was afforded the alkaline minerals to rob the copper sulphate of its acid. The figures show that solution of copper and iron progressed along nearly parallel lines, but that alumina was dissolved in increasing proportions with application of each succeeding lixiviant. The following table, given by Croasdale, illustrates the action of comparatively weak lixiviants when accompanied by circulation (virtually agitation), as compared with stronger, standing lixiviants:

4-Mesh Ore—24-Hour Treatment.

	Standing lixiviant		Circulating lixiviant	
Percent acid in lixiviant	Percent copper extracted	Lb. acid used per lb. copper dissolved	Percent Cu extracted	Lb. acid used per lb. copper dissolved
3.0	42.9	2.4	70.4	2.0
4.0	44.3	2.4	74.4	2.3
4.7	48.3	2.3	82.3	2.4
6.3	58.2	2.3	80.8	2.8
10.0	78.4	2.2	85.7	2.8

Crushing to 8-mesh increased consumption of acid without materially advancing extraction of copper, and the fine material resulting from further comminution interfered with percolation of solutions.

Similar experiments, made by the writer upon a garnetiferous ore carrying calcite, showed that ratio of acid consumption to dissolved copper was high when using very weak lixiviants. With increasing strength of lixiviant, acid consumption diminished, reaching a minimum with approximately a two-percent (by weight) acid solution, and then rapidly rose again with augmented strength of lixiviant and slowly advancing copper extraction. Building up the acid solution through successive additions of acid, until the total amounted to two percent, resulted in a slight saving of acid but required more time. These were laboratory tests, two pounds of fine ore being used in each case. The bottles were shaken at frequent intervals.

The use of partially neutralized lixiviants on fresh ore has a tendency to lessen acid consumption by utilizing to the full

extent any free acid left in the lixivium antecedent to deposition of the metal. This is one of the advantages in the counter-current system of lixiviation; but if acid content of the lixivium becomes too depleted, or completely neutralized, a portion of the copper is reprecipitated in the pulp. For this reason it is sometimes advisable to send lixivium to the precipitation department still containing a little free acid: it also prevents formation of basic iron salts, insuring a clean precipitate.

At the leaching works of the Arizona Copper Co., where certain tailing coming from wet-concentration mills was beneficiated, experience demonstrated the advantage of treating fresh material with a lixiviant high in copper and low in acid. The object was to obtain lixivium containing practically no free acid. The partly leached pulp was then given a second treatment, with a solution lower in copper and higher in acid, and finally with a fresh acid lixiviant. It was then washed. The ore being of porphyritic nature, presumably did not contain an appreciable quantity of calcite.

Dr. Gahl, in leaching tests carried out at Morenci (Arizona), found it economical to "leach in steps" (the principle just referred to as in use by the Arizona Copper Co.), and has described* a system of counter-current lixiviation.

At Anaconda it was found that the acid consumed when leaching mill-sand did not average to exceed 50 lb. of H_2SO_4 per ton of charge, and that the loss in salt (NaCl) escaping in solution discard was not more than one percent of weight of calcine leached. A solution carrying as high as 18 percent acid was employed in one test at Anaconda, using the alternate draining and flooding system, without any advantage being noted from application of this excessively high acidity.

The average amount of acid used in the solutions employed in the Ajo tests was 8.9 percent H_2SO_4, and the quantity consumed was 3.6 lb. acid per pound copper dissolved.

At the works of the Arizona Copper Co., 2.6 lb. of 52° B. acid (equivalent to 1.82 lb. 66° B. acid) is stated to have been used per pound of copper extracted.

Acid consumption at the Butte-Duluth plant is said to be

* "Leaching of Copper Tailings", Am. Electrochem. Society, New York meeting, April, 1914.

67.5 lb. of 60° B. acid per ton of ore, which amounts to 3.37 lb. per pound of copper extracted.

At Morenci, acid consumption was 3.5 lb. of H_2SO_4 per pound of copper recovered. In the Chuquicamata tests a gain of nine pounds of acid per ton of ore treated is reported, due to presence of sulphates in the raw material. The acid of the dissolved sulphates is set free in the electrolytic cells.

In estimating cost of leaching ore in more or less arid countries the quantity of water used becomes a matter of importance. At Ajo 128 gal. of lixiviant (1068.8 lb.) were circulated per ton of ore under treatment. It was found that 34 gal. (283.9 lb.) of solution were required to fill interstices in one ton of ore, after it had been saturated. At the Bullwhacker plant (Montana) the charge for an agitator was sixteen tons of ore and 32 tons of ten-percent acid lixiviant.

FOULING OF SOLUTIONS.

When solutions used in cyclic leaching become overcharged with salts, the common practice is to discard a certain amount, and to replace that thrown away by an equal quantity of fresh lixiviant. Discarded solutions are usually run to waste over scrap iron, to recover as much as possible of the valuable metals remaining in them. Solutions are not so apt to foul as might be supposed, for although they take up salts when strongly acid, they deposit these same salts in a more basic condition as the lixiviant becomes weaker. This is specially the case in counter-current cyclic-leaching.

Hydrolytic dissociation of ferric sulphate is a commonly observed phenomenon in dealing with leaching solutions. Lixiviant containing soluble ferric sulphate and little free acid, upon dilution gives up much of its ferric salt in a more basic form, with corresponding liberation of free acid. For this reason, when weak lixiviants are employed it is rarely necessary to discard any part of them.

At the Butte-Duluth works the same solutions were said to have been in use for more than three months without showing signs of excessive fouling. Drawing off slime from the first Dorr machine and settling it, and then sending the overflow from the

deposited slime to cementation launders, is said to have helped in keeping salts of iron and alumina out of the lixivium.

Iron, alumina, and calcium are the ordinary causes of fouling solutions, but ferrous and ferric sulphates, as well as aluminum sulphate, are solvents for copper oxide. Ferric sulphate also attacks simple copper sulphides and cuprous oxide, oxidizing them to cupric sulphate and dissolving copper present in this form. So the existence of these salts in leaching solutions is sometimes an advantage.

In Arizona, difficulties are said to have been encountered in leaching aluminous ore, because of the large quantity of acid consumed in taking up the soluble alumina. This was notably the case in attempting to leach slime at the works of the Arizona Copper Co. At the Gumeshevesky mine, in Russia, the alumina in the ore is said to have accounted for fifty percent of the acid consumed. At Ajo the solutions took up iron relatively as rapidly as they did copper, while alumina dissolved in increasing proportions with each succeeding application of lixiviant, reaching a maximum of about one percent of iron and alumina in the liquor. About half of the iron was in the ferric state.

Addicks states that in leaching experiments carried out by him at Douglas (Arizona) the resulting solutions contained as high as seven per cent alumina and three percent iron. In his opinion the real problem in ore-leaching in Arizona is the soluble alumina, and he suggests carrying the solutions so high in alumina that very little additional of this substance would be dissolved from the ore. He found that the quantities of alumina and iron mentioned above did not seriously interfere with electrolysis of such solutions, which others have thought might be the case.

When the agitation method of leaching is employed, less iron and alumina are dissolved, with higher extraction of copper, and less consumption of acid.* This is notably the case when agitating by means of compressed air.

Croasdale found the total weight of soluble material removed from the ore, in leaching at Ajo, varied from three to 3.5 percent.

* Mining and Engineering World, April 4, 1914, page 651.

THE SLIME PROBLEM.

The very fine material produced in ore crushing is generally regarded as a detriment in copper-ore leaching. When such fine ore is mixed with water it usually assumes the condition referred to as slime. The bad reputation slime has acquired, from the point of view of hydrometallurgists, is not wholly due to its quality of interfering with percolation, through packing in the leaching vats, because this can be overcome by resorting to agitation; but slime—especially aluminous slime—has the further property of fixing copper salts through adsorption (already mentioned in a previous section).

In the Clifton district (Arizona) the porphyry ore carries a mixture of copper sulphides and oxidized products resulting from decomposition of these sulphides. Some of this ore is greatly kaolinized and slimes badly in the wet-concentration mills. Slime produced in the Arizona Copper Co.'s mills is reported to carry 2.4 percent copper, and contains so much soluble alumina that lixiviation becomes practically impossible. It is sent to the slime pond and settled.

Slime produced in the Detroit Copper Co.'s mills, according to Gahl,* carries 1.24 percent copper, due to accumulation of oxidized copper minerals in this material. The sand tailing from the same mills has a very small copper content. Apparently oxidized copper minerals have a greater tendency to collect in the slime than is the case with sulphides. Gahl undertook to leach this slime by a system of counter-current lixiviation, and under the most favorable conditions recovered sixty percent of the contained copper. The lixiviant used was sulphuric acid and the copper extracted was thought to represent that portion existing in the oxidized state. Undoubtedly some ferric sulphate was formed during the treatment to which the slime was subjected, and this reagent contributed to the total of the copper extracted by decomposing some of the sulphides. The low percentage of extraction (sixty percent) probably was influenced by adsorption, due to the large amount of aluminous material present. The method of decantation employed is described in Dr. Gahl's paper.

* Loc. cit.

At the Butte-Duluth plant the slime problem had not been satisfactorily worked out, at last reports. As stated in a previous section, the slime was drawn off from the first Dorr machine and filtered through a bed of ore. The filtered liquors were sent to the cementation boxes, but considerable of value remained still locked up in the unwashed slime. It has been proposed to treat this slime in a continuous counter-current decantation plant. The slime makes up about thirteen percent of the ore treated, but carries very little colloids, as shown by the fact that the —200 product is granular and settles readily. Several screen tests made of the overflow material gave the following results:

Mesh	Percent
+80	2.6
+100	16.8
+200	34.4
—200	46.2

The slime overflow from the first and second Dorr machines assayed 0.35 to 0.48 percent copper, after washing.

At Anaconda, fine material was found to hinder percolation, and to cause imperfect washing and poor extraction. Ten percent slime when incorporated with mill-sand, even after roasting decreased percolation to such an extent as to make its treatment by mixing with sand very difficult.

Croasdale found, in the Ajo tests, that ore crushed to 2-mesh yielded two percent colloidal slime: crushed to 4-mesh, three to four percent colloidal slime that could be suspended in water. This slime assayed 4.5 per cent copper; whereas the original ore went 1.5 to 2.0 percent. An investigation of the tailing disclosed the fact that colloidal slime absorbs, or retains mechanically, as much copper as is held by the coarse material, and the further fact that the quantity of alumina increased in the fine material. Whereas acid could be readily washed out, removal of the copper was much more difficult, indicating mechanical retention of the metallic salt by the slime. Washing the tailing with 1500 gal. (6.25 tons) of water per ton of ore failed to remove the acid-soluble copper, which remained as high as when one tenth of the quantity of water was used. It is evident, therefore, that the property possessed by argillaceous substances, and col-

loids, of absorbing and retaining mineral salts, may be an important factor in leaching crude oxidized porphyritic ore by means of sulphuric acid.

TIME REQUIRED FOR BRINGING COPPER INTO SOLUTION.

Factors affecting speed of solution of copper from an ore are: character of the ore; fineness of comminution; method of leaching adopted; strength of solvent; and temperature of lixiviant. An ore which has been ground fine, or the permeability of which has been enhanced by roasting, must necessarily be more quickly acted upon by solvents than when treated in a coarser, or unroasted condition. Heating the pulp, and applying agitation, also increase speed of solution.

At the Butte-Duluth works when Dorr machines were employed, it is stated that forty minutes contact with acid solution in the first four machines gave an extraction of between 85 and 90 percent. In the original experiments, the results from which led to introduction of Dorr machines at this plant, it was found that with hand-screened ten-mesh product about ninety percent of the copper could be extracted in twenty minutes. Also less iron and alumina were dissolved, and acid consumption was reduced.

At the Bullwhacker plant, ore carrying two to four percent copper, when ground to thirty mesh and treated in a Hendryx agitator, is said to have given up 97 to 98 percent of its copper after fifteen minutes' treatment. When ground to 16-mesh, the extraction is stated to have been 92 to 95 percent.

At Anaconda, in percolating roasted sand-tailing containing 0.713 percent copper, treatment lasted six days, although the material percolated very readily.

At Ajo, where a solvent containing ten percent or more H_2SO_4 was employed, it was found that from 75 to 90 percent of the total copper could be extracted by the first application of lixiviant in from 36 to 48 hours. The average leaching period was three days eight hours, and subsequent washing required ten hours.

In the Chuquicamata experiments the leaching cycle comprised six days, during two days of which the ore was under acid.

In treating a garnetiferous ore carrying considerable chrysocolla, employing a six percent sulphuric acid lixiviant and agitating by means of compressed air, 86 percent of the copper was extracted in four hours. This ore had been ground to sixteen mesh and was treated without being roasted.

PERCENTAGE OF EXTRACTION.

It has been observed that the amount of metal remaining in tailing resulting from treatment of low-grade ore is apt to be a very constant factor, irrespective of the value of the original material. This explains why percentage of extraction may fall off in proportion to decrease in grade of ore. Croasdale found in making analyses of some tailing that practically all the copper remaining in it was in soluble form, and that extremely fine material carried more copper than some of the coarser sizes. Washing such tailing with large quantities of water did not remove the contained copper, even when the presence of either copper or acid was not indicated in the final washwater.

Attention has been repeatedly called to the fact that certain clays, as well as porous, carbonaceous, and colloidal substances, possess the power of extracting metals from very dilute solutions. A clay (slime) has an enormous number of individual particles, with large aggregate surface, within small space. Sand, on the other hand, consists generally of rounded particles, which present the least amount of surface compared to volume of mass. For this reason, slime tailing is apt to carry more metallic salts than is sand-tailing; and therefore the gangue of an ore must be considered in respect to its adsorption qualities as well as its acid-consuming properties.

If a one-percent aqueous solution of copper sulphate be poured upon a thin layer of pure kaolin, the filtrate, after some hours, will be found to contain very little copper. At one time an attempt was made at Butte to de-copper the mine waters by passing them through clay filters, but the clay used was not suitable to the purpose.

As an example of percentage of extraction obtained in leaching unroasted porphyritic ore by percolating with a sulphuric acid lixiviant, the Ajo tests may again be referred to. In this

instance the total amount of copper extracted was given as 77.8 percent. Soluble copper remaining in the tailing was 14.7 percent, leaving 7.7 percent as insoluble.

Another instance of results achieved by percolation-leaching is derived from the Chuquicamata experiments, where 89.6 percent was claimed.

At Anaconda, in percolating mill-tailing sand, the results from two months' operations showed copper recovered amounting to 85.4 percent, and silver 91.1 percent. It is expected that under conditions which should apply in a large plant a recovery of 85 percent could be counted upon, with a probability of reaching 86 or 87 percent. This would leave about 2 to 2.25 pounds copper per ton of tailing.

In investigating the relative amounts of extraction in different parts of a vat at Anaconda, samples were taken from the top and bottom of a charge. These showed in one case a lesser extraction, amounting to seven percent, at the bottom than at the top. In another case extraction from the bottom layer was two percent less than from the top; and in a third instance the results were reversed.

Recoveries obtained by leaching with agitation instead of percolation are given below.

Extractions at the Butte-Duluth plant, since the introduction of the Dorr apparatus, have been variously reported as from 85 to 90 odd percent. Herzig* gives some interesting details concerning the preliminary experimental tests on Butte-Duluth ore with the Dorr machines.

Experimental Dorr Tests.

Pulp assays	Contact with acid	Washing	Extraction	Strength of acid
— 4-mesh.... 2.98% Cu.	7.2 min.	1.8 min.	75.75%	7.0%
— 4-mesh.... 2.52 " "	36.0 "	9.0 "	61.2 "	7.8 "
— 9-mesh.... 2.66 " "	36.0 "	9.0 "	82.4 "	7.0 "
— 9-mesh.... 2.64 " "	17.33 "	4.33 "	83.4 "	9.0 "

There is said to be practically no colloidal slime in this ore, the —200 mesh material settling reasonably fast. Of the total charge about 13 percent passed off as slime in the overflow from the first Dorr machine.

* Loc. cit.

At the Bullwhacker plant, where the Hendryx agitator is used, 97- to 98-percent extraction is said to have been effected in fifteen minutes when treating 30-mesh material assaying 2 to 4 percent copper. With 16-mesh pulp, the extraction is said to have been 92 to 95 percent. From another source it was learned that when continuous decantation was tried the extraction was 90 percent in 30 minutes.

Mention has already been made in a foregoing section of 78.2 to 84.8 percent extractions having been obtained from garnetiferous ore ground to sixteen mesh and carrying about two percent copper. These extractions were effected, with help of air agitation, in four hours, the lixivium being remarkably free from iron. The same ore when subjected to the slower percolation-treatment gave up its iron freely.

When lixiviant is left in contact with ore after free acid has disappeared, some of the copper is liable to be precipitated.

WASHWATER.

The coarseness of pulp undergoing leaching determines the quantity of water required to wash out valuable solutions retained in the pores and interstices. To wash a coarsely-ground ore-charge requires comparatively little water; to free a slime from its contained liquors necessitates resort to continuous decantation, or filtering, with inevitable accumulation, or wasting, of washwater.

Recourse has been had to various schemes for disposing of accumulated washwater. In arid regions advantage is sometimes taken of rapid evaporation caused by climatic conditions, and liquors are allowed to flow over appropriately constructed evaporating frame-work. In other places a definite part of the washwater is run to waste over scrap iron.

At Anaconda it was found that to effect a reasonably good wash of mill-sand after lixiviation, an amount of water equivalent to forty percent of the weight of the sand was required.

In treating 4-mesh porphyry ore at Ajo it took water amounting to fifteen percent of the weight of the ore (36 gal. per ton) to fill interstices and to cover charge in the vat. This was in addition to the water absorbed by the ore, which was eleven

percent of its weight (26.4 gal. per ton) and remained with the tailing. The total washwater used per ton of ore treated was 268 gal. (2238 lb.).

At the Butte-Duluth plant the washwater used in the last Dorr machine was run to waste over scrap iron.

REMOVAL OF TAILING.

Where leaching is done by percolation, removal of tailing from vats constitutes an item of considerable expense. Sand tailing will not run by gravity unless it contains a high percentage of water, and therefore must be dug out, or sluiced. At large lixiviation works special machines are used for this purpose, and plows constructed of cast iron, steel, or high silicon iron have been recommended.

At Anaconda it was found that 7,000,000 gallons of water in 24 hours would carry away all the tailing which two men could sluice out of five twelve-inch gates placed in the bottom of a vat. Probably a much less quantity of water might have answered. The greatest difficulty was experienced at the start when the sand caved and filled the holes. It was found that two men could sluice out 400 tons of sand-tailing from one vat in about five hours.

At the Bismark cyanide mill in the Black Hills, where ore was crushed to 4-mesh and percolated in vats, the tailing was shoveled through four gates in the vat bottom. To discharge a 200-ton vat, and tram the tailing about 100 yards to the dump, required about seven hours.

DISSOLVING THE SILVER.

The quantity of precious metals in low-grade copper-ore suitable for leaching is generally negligible, but sometimes the extraction of small amounts of silver and gold becomes of paramount importance. Many methods have been devised with this object in view, some of which have been applied upon a commercial scale.

At Anaconda the mill-tailing treated carried 0.55 oz. silver per ton. This material was given an oxychloride roast in a modified McDougall furnace, and the roasted pulp was leached

with strong brine. An oxidizing roast alone rendered only half of the silver soluble, and the copper extraction was not as good as when oxychloride roasting was employed. The recovery of silver by this means was 93.4 percent of the amount in the original tailing.

The method finally adopted for removing silver from the leached pulp was simple and efficacious. When lixiviation was finished, and washing began, a quantity of salt (NaCl), amounting to one percent of the weight of the pulp, was spread over the top of the charge just before the washwater went on. The strong brine traveling down through the charge removed practically all of the silver chloride remaining from the previous lixiviation. The first brine flowing from the vat was sent to the solution reservoir, to replace discarded solution, and in this way very little salt was lost in the washwater. It was noticed at Anaconda that the silver dissolved as AgCl in the briny lixiviant had a tendency to precipitate, to some extent, on the lead linings of the vats. The lead became rapidly coated and precipitation of silver then ceased.

The lixiviums on cooling, or upon dilution with water, deposited a part of their contained AgCl, and some of this substance collected in the bottom of the solution vat. A portion of the AgCl was precipitated in the tailing through dilution of the residual lixivium by washwater in washing.

All of the silver in the leach liquors was deposited on scrap-iron in the precipitation boxes.

An attempt was made to leach the roasted mill-tailing with sulphuric acid lixiviant without addition of salt, to ascertain whether or not recovery effected in this way would warrant running the resulting liquors to waste after precipitating the copper. If the copper could be dissolved as sulphate, then upon applying salt to extract silver, the amount of copper still to be taken up would be comparatively small. As less iron would go into solution, the saline liquors would be freer from impurities; also consumption of salt would be decreased. It was found that only half the quantity of copper was dissolved as was the case when using a briny lixiviant, and that more time was required. In this connection it will be recalled that Hunt* found that calcined

* Trans. Am. Inst. of Mining Engineers, Vol X, page 18.

sulphide ore contains cuprous compounds which are insoluble in water or sulphuric acid, yet are dissolved by a strong solution of salt.

Plattner showed that gold, like silver, is chloridized when pyritous ore containing it is roasted at a low red heat with common salt. An aurous chloride is apparently formed, which, in the presence of chloride of sodium, has a considerable degree of stability, although it is decomposed at high temperatures. This chloride of gold is insoluble in water and but slightly soluble in brine. It is readily soluble in hyposulphite of soda or lime.*

REMOVING COPPER FROM SOLUTIONS.

The several methods of precipitating copper from liquors obtained through ore lixiviation may be considered under four heads:

Electro-chemical precipitation, generally by means of some form of iron, or by a galvanic couple.

Chemical precipitation, using some reagent capable of throwing down copper from solution in an insoluble form.

Electrolytic deposition, through application of electric current generated by a dynamo.

Deposition of a copper salt by means of alteration of pressure or temperature.

A choice of one or other of these methods will be controlled by local conditions, such as availability of some particular precipitant in the place where it is to be used, and its adaptability to the leaching process employed, or its effect upon the solutions. The final product desired may also have influence, as the choice of precipitants will be narrowed down to those yielding that product; but in most cases the necessity for selecting a reagent which will permit re-use of the lixiviant on a fresh batch of ore will prove to be the deciding factor.

There are many solvents which may be employed for bringing the cupriferous content of an ore into solution, and the first stage of the treatment—that is, solution of the metal—is the simplest. Even separation of the metal-bearing liquors from the leached pulp, although not always an easy operation, still presents mostly mechanical difficulties. Transferring the metal

* Trans. Am. Inst. of Mining Engineers, Vol. X, page 13.

from its dissolved state to some commercial form, without sacrificing the lixiviant, and without incurring very considerable expense, is a more difficult matter.

Probably the oldest method resorted to by metallurgists for depositing copper from solution was passing the lixiviant over metallic iron, and it has been recently stated that this is the only method of precipitating the metal which has been a demonstrated success. While this statement is correct as to the past, it is improbable that iron-precipitation will much longer hold its supremacy, even in the case of sulphate and chloride solutions overcharged with deleterious salts. There are means of bringing copper into solution other than with the help of strong mineral acids, and some of these methods are not without promise. Hydrometallurgy of gold and silver was not a pronounced success as long as one of the strongest reagents known—chlorine—was employed. It was when the selective action of a weak alkaline solvent was introduced that treatment of gold and silver ores by so-called wet methods of reduction assumed its present importance.

PRECIPITATION WITH IRON.

Iron has been employed in different forms for precipitating copper. Often it is found advantageous to use up accumulations of old scrap or discarded tin cans for this purpose; but when such material is not available in sufficient quantities, cast iron in form of plates, bars, or granules has been used. Precipitation of copper by means of sponge-iron was formerly known as the Aas process, and is described in the Berg- u. Hüttenmännische Zeitung for 1862.

Iron is adapted to precipitation of copper in most processes, but not in all. The advantages in its use are extreme simplicity, and recovery of the metal in a concentrated form. One disadvantage is that it fouls the solutions, so that portions of these must be discarded when it is desirable to return them to the cycle of operations. This becomes a serious objection when valuable reagents, such as NaCl, are lost in the wasted liquors.

At Anaconda it was found necessary to discard one quarter of the solution each time it was used, to obviate excessive accumulation of ferrous sulphate.

Experience gained at the Gumeshevesky mine (Russia) indicated that granulated cast-iron is very much better than plates of the same material for precipitating copper. Granulated iron has a larger surface per pound of material, and as it can be used in rotating trommels, the granules are kept bright through attrition. This produces rapid action, and saves labor entailed in cleaning plates and pieces of scrap.

Granulated iron can be produced by shattering a small stream of molten iron by means of a steam jet and cooling the granules in water. At Ajo a tube mill was employed for precipitating the copper. With a neutral solution, one pound of copper was precipitated per pound iron consumed. The precipitate assayed 73.6 to 86.8 percent copper.

At Anaconda sponge-iron was found to possess advantages over scrap, and it affords independence of the scrap-iron market. It can be made from calcines which contain about fifty percent iron. The reduction of ferric oxide begins at 420° F. (216° C.) and is completed at 1075° F. (580° C.). With ferrous oxide, reduction begins at 1300° F. (704° C.). Croasdale states that it is feasible to metallize calcines for use in copper precipitation for about $5.00 per ton of metallic iron.

Experience has shown that retorts and muffle furnaces are not adapted to making sponge-iron. Experiments with the Wedge roasting furnace at Douglas (Arizona) and with a McDougall roasting furnace at Anaconda were unsatisfactory. There is some difference of opinion as to the relative merits of continuous furnaces and the intermittent type. After considerable experimenting, the Bruckner furnace was adopted for this purpose at Anaconda, where twenty tons of sponge-iron were made per diem with a cylinder 8.5 by 12 feet. Fuel consumption was: coal, forty percent of weight of calcine, in addition to twenty gallons of fuel-oil. The best results were attained at a temperature of 1680° to 1700° F. (916° to 930° C.). One pound of copper was precipitated by 1.5 pounds of this sponge-iron.

At Anaconda the lixivium from the 80-ton experimental leaching plant averaged: Cu, 1.91%; $Fe_2O_3 + Al_2O_3$, 3.88%; NaCl, 8.3%; Ag, 0.634 oz. It was not found economical to increase the copper content of the lixivium much above the percentage given. At 30° C. (86° F.) this solution, carrying 0.7

percent H_2SO_4, was reduced by clean fresh iron to about 0.1 percent copper, when circulating at the rate of 8 to 10 gal. per minute through 150 feet of launders. The launders were 3 ft. wide by 2.5 ft. deep, and had false bottoms 4 in. above floor. There was a settling tank at the end of the launders. The copper did not attach itself to wrought iron and therefore this did not have to be cleaned, but with cast-iron scrap a layer of metal quickly formed, necessitating brushing and scraping before the iron was fit for further use. About 1.15 pounds of iron were consumed per pound of copper thrown down. The precipitate assayed 75 to 85 percent copper. After testing at these works various methods of precipitation, preference was given to the use of sponge-iron.

Iron replaces copper which is in solution as sulphate, because of its greater solution pressure. After copper has begun to deposit on iron, innumerable small galvanic couples are formed, which further precipitation of metal from solution. The action set up between members of a galvanic couple is the more intense the further the elements are apart in the Volta-tension series, though this is influenced by the character of the liquor in which they are immersed. As carbon is closer to the negative end of the series than copper, therefore the effect of an iron-carbon couple is more energetic than iron-copper. If coke is placed in contact with iron in the precipitating boxes, copper is taken out of the liquor in a much shorter time than where iron alone is employed.

Precipitation of copper by means of natural and artificial sulphides has been described by Croasdale;* but experiments carried out at Ajo, using sulphides of iron, were not successful, due in a measure to tardiness of reactions.

CHEMICAL PRECIPITATION.

The opinion is held by some metallurgists that chemical precipitation of copper, which has been obtained in soluble form through leaching ore, will eventually be the means adopted in operations of this nature, in cases where electrolysis is not applicable. One objection to precipitation of copper through chemical reagents is that such methods generally produce an

* Eng. and Mg. Journal, April 11, 1914.

intermediate product from which commercial metal must be subsequently recovered at further expense.

Hydrogen sulphide may be taken as an example of a chemical reagent which has often been employed for removing copper from lixivium. It possesses such manifest advantages as a precipitating agent that recourse has been had to it repeatedly; still that method of precipitation has not developed in this country on a large scale; and its use presents admitted difficulties. Nevertheless it has been found possible to precipitate copper from weak solutions with the help of hydrogen sulphide gas, when precipitation by iron was no longer commercially profitable. In another instance, hydrogen sulphide gas was regularly employed in precipitating copper from mine waters carrying 0.1 to 0.15 grams copper to the litre. In this, as in many other chemical processes, much depends upon applying the reagent in a manner suitable to the object to be attained.

An advantage which hydrogen sulphide possesses is that it does not carry undesirable elements into the leaching liquors, as is the case with iron; at the same time it sets free (regenerates) the acid which was combined with copper in the lixivium. When copper is present as sulphate, theoretically hydrogen sulphide gas liberates 1.55 pounds H_2SO_4 for every pound of copper thrown down as CuS, thereby regenerating the acid lixiviant in a simple and effective manner. Copper sulphide settles readily from solutions and may be filter-pressed, bricked and smelted, or manufactured into blue-vitriol. Copper sulphide contains 66.5 percent copper, which will average fairly well with cement copper obtained through precipitation with iron.

Experiments made at Anaconda, using hydrogen sulphide gas as precipitant for copper, gave inferior results as compared with sulphur dioxide and sponge iron, largely owing to inefficient absorption of the gas. From description of the methods used in applying the reagent, and of manufacturing the gas, it seems possible that a different conclusion might have been reached with further experimentation. The gas was generated in a lead-lined drum through the action of sulphuric acid on iron matte ground to 4-mesh, 2.4 pounds of acid being required to generate gas for precipitating one pound copper. Percentage of efficiency for acid was about 62 percent—for FeS, about 54. The

gas was passed through 3.5 feet of cupriferous solution in large bubbles. Filter-pressed cakes of precipitate carried 48 percent moisture. The dried material assayed: Cu, 58%; S, 29%; Ag, 69.5 oz.; Au, 0.04 oz. A point mentioned in favor of employing matte in generating hydrogen sulphide is, that its copper content is enriched by removal of iron and sulphur.

There are other ways of generating hydrogen sulphide gas commercially. Among these is decomposition of wet calcium sulphide by means of carbonic acid gas, and another is, passing producer gas over heated pyrites. In the latter process the ignited carbonic oxide gas attacks the pyrites, sulphur combining in part with free hydrogen produced through decomposition of steam, in part with the hydrogen of the hydrocarbons. Carbon is set free. Illuminating gas has been used in the same way as producer gas.

Different methods have been suggested for bringing cupriferous solutions and hydrogen sulphide gas into effective contact. Passing large bubbles through the liquors does not produce good results. Croasdale proposes the use of a porous diaphragm (burlaps, or perforated sheet lead, or silica sponge) and allowing small bubbles of gas to pass through a shallow stream of solution three inches deep (not over six inches). He considers a launder with shallow stream more efficient than a vat.

Other methods have been tried and appear to have given satisfaction. For instance, a tower provided with shelves, which permit cupriferous liquors introduced at the top to trickle down through an atmosphere of hydrogen sulphide gas, may be advantageously used for precipitating purposes. All escape of the gas is shut off as the top is hydraulically sealed, as well as the bottom, and copper is rapidly removed from the liquors as they fall down from shelf to shelf. The metal is said to be wholly precipitated from solutions before the bottom is reached. The tower is connected above and below with the hydrogen sulphide generating apparatus. With regard to use of hydrogen sulphide gas, it might be incidentally mentioned that in case of poisoning, alcoholic stimulants, or wine, should be administered. Hydrogen sulphide causes the blood to flow slowly: alcohol as a stimulant counteracts this effect.

Another gaseous reagent which has a number of advocates, and is adaptable to removal of copper from solution, is sulphur

dioxide. Precipitation with this reagent is based upon the fact, that when copper sulphate is heated in a closed vessel under pressure, in presence of sulphur dioxide, the copper salt is reduced to metallic copper and sulphur dioxide is oxidized to sulphuric acid. Recovery percentage of the copper increases with temperature, and decreases as concentration rises. It is not necessary that copper should be present as sulphate; chloride solutions are also amenable to this method of recovery.

The Weidlein process* is based on reduction of cupric sulphate by means of sulphur dioxide gas, and has been for some time under investigation at Wabuska (Nevada); but results have not yet been made public.

The best account of recent experimental work, in the way of precipitating copper from solutions by means of sulphur dioxide gas, is that given by Messrs. Laist and Frick.† These tests were carried out at Anaconda, and the results are set forth with a wealth of instructive detail characteristic of the source from which it comes.

The lixivium used in these precipitating tests carried its copper and silver as chlorides in a briny solution. The gas contained ten percent by volume of sulphur dioxide and was drawn from a McDougall roaster. The best results were obtained when the cold lixivium was saturated with sulphur dioxide gas under a pressure of 15 lb. per sq. in., and the saturated liquor then heated under 20 lb. pressure. After a short boiling it was cooled to 60°-70° F. (16°-21° C.). The white crystalline cuprous chloride separated readily.

In this process the theoretical equivalent of 1.55 lb. of H_2SO_4 should be recovered for each pound of copper precipitated as Cu_2Cl_2; but, as a matter of fact, 2 lb. to 2.5 lb. acid were produced, due to reduction of ferric salts and catalytic action of Cu_2Cl_2.

Results from a number of 500-lb. runs are tabulated in the original paper, showing an extraction of 81.75% copper, with tail solution carrying 3.91% H_2SO_4, obtained from a lixivium containing 2% copper and 0.5% H_2SO_4. Extraction of silver was 100 percent.

* U. S. patent No. 1,089,096, March 3, 1914.

† Trans. Am. Inst. Mining Engineers, Salt Lake meeting, 1914.

Precipitation from Anaconda solutions by means of sulphur dioxide gas was found to present no difficulties, and it was thought that copper could be recovered by this method for about $10.00 per ton, without allowing credit for regenerated acid. The main expense incurred was in heating the liquors. However, under local conditions, simple precipitation by means of sponge iron was thought to present advantages over the use of sulphur dioxide, and so experimentation with the latter process was abandoned. Where electrolysis cannot be used owing to high cost of power, rapid fouling of solutions, or presence of chlorides, it was thought that precipitation by means of sulphur dioxide might be a good alternative. The process was found to be entirely practicable.

In the original paper, figures are given showing that by roasting 100 tons of certain sulphide concentrate, about 80 tons of sulphur dioxide gas would be obtained. Fifty tons of this gas could be absorbed in treating copper solution, and this will precipitate about 100 tons of copper in form of cuprous chloride. The iron in the roasted concentrate, when converted into sponge iron with copper equivalent of 0.8 to 0.9 on Cu_2Cl_2, could be used to recover metallic copper from the Cu_2Cl_2. Theoretically, 0.44 lb. pure iron are required per lb. copper precipitated from Cu_2Cl_2.

Depositing copper from solutions as cuprous chloride by means of sulphur dioxide, followed by treatment of the precipitate with sponge iron, makes an effective combination. The advantages are: utilization of roaster gases; economy in iron used for precipitation, by extracting it from roasted material; and recovery of copper from solutions in concentrated form.

As another possible chemical reagent for precipitation of copper, reference is made to the statements of Mr. Claude Vautin,* who calls attention to a new application of ammonia for this purpose. Mr. Vautin states that sulphate of copper liquor, treated by ammonia according to a certain method of procedure (not given), yields its copper as precipitate in form of basic sulphate, which is easily collected, washed, and dealt with for metal recovery.

* Bull. Inst. Mining and Metallurgy, May 21, 1914.

ELECTRICAL DEPOSITION OF COPPER.

Just what part electrolysis is destined to play in removal of copper from cupriferous lixiviums on a commercial scale has not yet been definitely determined. Much can be said in favor of applying this means of extracting the metal after it has been brought into soluble form; but, on the other hand, several prominent metallurgists consider the problems involved so serious that they have turned to other means of precipitation. The subject is worthy of further study on the part of those equipped for such investigations.

Whereas electrolytic refining is now applied on an enormous scale, and electrolytic extraction at first thought appears to be a very similar operation, still conditions under which the two processes are carried out are very different. In electrolytic refining the metallic content of the bath is kept practically constant: metal is merely transferred from anode to cathode with small expenditure of power. In electrolytic extraction, metal is being constantly removed from a complex electrolyte, with important alterations in factors which affect passage of the electric current.

Means for remedying the difficulties encountered in applying electrolysis to extraction of metal from cupriferous solutions are being sought, and some success has been reported. The old idea of attempting to extract all the copper from an electrolyte has been abandoned, and metallic content of the liquors is now held at a more or less constant point by rapid circulation through both ore-leaching vats and electrolytic cells. In this manner it is attempted to take up copper from the ore as fast as it is deposited on the cathodes. As far as known, this method was first applied on a commercial scale at the Butte-Duluth plant.

As a much greater expenditure of power is required to extract copper from cupriferous solutions than to refine copper anodes, it has been attempted to counterbalance this difficulty by introducing depolarizers into the electrolyte. Mr. R. R. Goodrich* mentions the fact, that when sulphur dioxide gas is used as a depolarizer in electrolyzing copper sulphate solution, the theoretical voltage required to operate the cell figures out as a negative quantity (— 0.15 volt). To quote from Mr. Goodrich's

* Bull. Am. Electrochemical Soc., New York meeting, April, 1914.

paper: "This would indicate that with such a current density as to secure anode efficiency of 100 percent, if this could be realized, the electrolytic cell would no longer require an impressed voltage, but would become a primary cell". That something more than theoretical calculations has been accomplished along these lines, is evidenced from the statement made by Mr. L. Addicks.† Mr. Addicks reports that at Douglas (Arizona), using carbon anodes and ferrous sulphate as a depolarizer, eighty-percent current efficiency has been achieved, with about 2.5 lb. cathode copper deposited per kilowatt-hour. To produce such results, probably very low current density was employed; and this raises the question of size and cost of plant necessary to yield a given quantity of cathode copper under these conditions.

Important factors in electrolytic deposition of copper are: cost of power; material for anodes; and composition of electrolyte. These subjects will be taken up separately further down; but with reference to composition of electrolyte it can be mentioned here that, as far as reported, electrolysis of cupriferous chloride solutions has not yet been successfully carried out on an extended scale. Presence of chlorides in sulphate solutions undergoing electrolysis has repeatedly caused trouble. Chlorine may get into the electrolyte through presence of soluble chlorides in ore, or in the water employed. It was largely owing to difficulties encountered in electrolyzing chloride solutions that this method of treatment was not considered at Anaconda. At Chuquicamata electrolysis will be the method adopted for precipitating copper; and as the lixivium carries considerable chlorine, it is proposed to free the solutions from this element, before sending them to the electrolytic cells, by treatment of the neutral lixiviant with metallic copper in rotating cylinders.

Solutions derived from leaching low-grade ore usually carry only a small quantity of copper, and practical difficulties are encountered in trying to increase the content. Weak cupriferous solutions offer much resistance to passage of electric current, and it has been largely owing to commercially unsuccessful attempts made to electrolyze such solutions that this method of recovering copper has not met with more favor. A practical way out of this difficulty would seem to be chemical precipitation of the metal

† Eng. and Mg. Journal, January 9, 1915, page 92.

from weak lixivium, followed by electrolysis of the precipitate thus obtained. Several ways of accomplishing this have been tried, and others naturally suggest themselves.

COMPOSITION OF THE ELECTROLYTE.

Sulphate lixiviums drawn from leaching vats for treatment in electrolytic cells have, usually, small copper content. The average lixivium will probably not exceed two percent copper, when washwater is included. Sulphate lixivium appears to reach a point of saturation for copper, and then to take up other elements with more avidity than the copper. An illustration of this phenomenon was shown in some leaching tests made on a garnetiferous ore with help of air agitation. It was found that after two-hours' treatment the lixivium carried 1.4 percent copper: continuing agitation another two hours (four hours in all) raised copper content of the lixivium only to 1.5 percent. In another instance, when a stronger acid lixiviant was employed, the lixivium contained 2.6 percent copper at end of two hours' agitation, but lost copper in the second period of two hours, although free acid in the lixiviant was still above five percent. Copper was evidently precipitated by ingredients contained in the charge, and in a form which was not soluble in sulphuric acid.

In percolating ore with sulphuric acid lixiviant, a number of bases are taken up by the solvent, which complicate subsequent electrolytic extraction. Foremost among disturbing elements is iron. As everyone knows, who has had experience in electrolyzing ferruginous copper-sulphate solutions, ferrous iron is oxidized to the ferric state at the anodes, which is again reduced to ferrous condition at the cathodes. These reactions give rise to great waste of current when iron salts exist in the electrolyte in considerable quantities without presence of a reducing agent.

To deposit copper in metallic form by electrolysis from sulphate solution, oxygen is, of course, liberated at the anode, and this oxygen will necessarily combine with any element present which is susceptible of being raised from a low to a higher oxide. For this reason iron may be used as a depolarizer, provided it can be kept in the ferrous condition. This may be done by charging the electrolyte with sulphur dioxide gas.

Addicks* has called attention to the use of lixiviants (as well as electrolytes) charged with sufficient quantities of impurities to restrict solution of additional salts of like nature in ore leaching. Addicks states that electrolytes carrying as high as seven percent Al_2O_3 have been employed, and that solutions containing three percent Al_2O_3 and three percent iron give no trouble in depositing copper under conditions specified. It is assumed, (although not so stated by Mr. Addicks) that this iron is kept in the ferrous state by some reducing agent present in the electrolyte, thus eliminating danger from action of the ferric salt at the cathode. The lixiviant therefore acts in the ore-leaching vats by virtue of its contained aluminum sulphate (probably assisted by free acid), and as aluminum sulphate is not affected as are iron sulphates by conditions prevailing in copper deposition, no trouble is experienced from this source in the electrolytic cells. Kerl mentioned, fifty years ago, aluminum sulphate as a solvent in leaching copper ore; and recently a German patent was taken out for a process designed for copper extraction, the basis of which is successive applications of aluminum sulphate and sulphuric acid. Copper is then recovered from the lixivium in sulphate form by evaporation and crystallization, whereby a commercial product is obtained without help of chemical precipitation of electrolysis.

At Ajo the porphyritic ore which was subjected to leaching contained on the average 1.45% Cu, 14.3% Al_2O_3, and 4.2% Fe. From this was derived a nearly neutral lixivium, which varied between 2.22% and 2.9% Cu, 0.47% and 0.73% Al_2O_3, and 0.42% and 0.70% Fe. The liquors were sent to precipitation boxes and run over iron.

At the Butte-Duluth plant lixivium from the Dorr machines which was sent to the electrolytic cells is said to have assayed about six percent free acid and from four to six percent copper. It left the cells containing about eight percent free acid, and from 1.5 to 2.0 percent copper. The solutions were then brought up to ten percent free acid and pumped back to storage tanks, from which they again flowed on the ore. By this method copper content of electrolyte was constantly renewed through extraction of fresh metal from the ore. Thus advantage is taken of the

* Bull. Trans. Am. Inst. of Mining Engineers, Salt Lake meeting, 1914.

well-known facts, that the richer the copper content of electrolyte, and the more rapidly it is circulated, the better are the results obtained for power expended. This is to be expected, for by these means, supply of copper ions to the cathodes is facilitated.

In preliminary tests made on Chuquicamata ore, after more than a year's work with the same solution (discarding only enough to take care of excess acid), the following impurities were found to be present:*

	Grams to Litre.
Fe	3.71
MgO	3.32
Al_2O_3	1.61
Na_2O	21.6
K_2O	5.0
HNO_3	4.0
CaO	0.8

This, it is assumed, would represent the electrolyte after passing through the cells, if copper content and sulphuric acid were added.

At Chuquicamata the electrolyte will enter the first depositing cell containing about five percent copper and 2.5 to 3.0 percent free acid. It will leave the last cell of cascade carrying 1.5 percent copper and from eight to nine percent free acid.

ELECTRODES.

Electrodes used in depositing copper from sulphate solutions have been constructed in various shapes and from different materials. In the most common type of cell, plain sheets are hung vertically in rectangular tanks, imitating electrolytic refining practice. But also movable, and fixed, horizontal electrodes, as well as rotating anodes and cathodes, have been used. Each type of cell presents certain advantages.

A primary requisite in an electrolytic cell is to bring copper ions into contact with the electrolyte as rapidly as possible. Evidently in effecting this, circulation of electrolyte must be brought

* E. A. Cappelen-Smith, Eng. and Mg. Journal, April 25, 1914, page 865.

about by some means. If circulation is produced by accelerating flow of electrolyte through the cells, the plates are usually hung vertically and parallel with the course of the stream. Other arrangements of vertical electrodes have been suggested, with the object of forcing the liquors against the faces of the plates, and of preventing accumulations of partially electrolyzed solution in the path of the electric current.

Moving horizontal anodes have been advocated from time to time, both at home and abroad, and patents have been obtained for such apparatus. One of the objects aimed at in such cells is to shake off the oxygen bubbles as they form, and thereby reduce the oxidizing and polarizing effects of that gas. Agitation of electrolyte is also produced, and if the cathode is placed below the anode, the heavier (cupriferous) part of the solution collects where it is most desired to have it. Cells of this type have been experimented with considerably in this country. Siemens & Halske employed a cell with horizontal electrodes in the process bearing the name of that firm.

Cells embodying the principle of rotating electrodes have frequently appeared. Electrodes can be rotated at any desired speed, bringing about a most efficient contact between cathodes and copper ions. It is remarkable with what high current density and power efficiency such cells can be operated. In some cells of this character centrifugal action plays an important part.

Action of rotating cathode with respect to physical properties of the deposited copper, speed of rotation, current density permissible, current efficiency, etc., have been discussed in a paper read before the American Electrochemical Society by Mr. C. W. Bennett.* Another paper on the same subject ("Rapid Refining of Copper with a Rotating Cathode") was read before the same society by Messrs. Bennett & Brown at the meeting of the society in September, 1913.

In regard to material from which electrodes are made, copper sheets are usually employed for cathodes. These, called starting sheets, are generally made at the works. At the Butte-Duluth plant the cathodes are copper sheets measuring two feet by three feet, and weigh at the start between two and three pounds. There are 640 of these sheets in the cells, and it is

* Trans. Am. Electrochem. Soc., Vol. XXI, pp. 253-274.

expected to deposit from eight to ten pounds of copper on each sheet daily.

For anode material various substances have been experimented with—ordinary commercial lead, lead-antimony alloys, carbon, graphitized carbon, and fused magnetite. Each has its advocates.

Lead anodes are more or less corroded through oxygen set free at that electrode by the current. A scale of brown peroxide of lead forms which in a measure protects the metal from further oxidation. As this substance is a fairly good conductor of electricity (much better than graphite), it does not seriously interfere with the process. When sulphur dioxide is used in the bath as a reducing agent, no PbO_2 is deposited on the anodes, but in its place a coating of $PbSO_4$ appears. This sulphatizing action is said to be less rapid than peroxidation when SO_2 is not used.

Laszczynski* has sought to prevent anodic oxidation of cations by wrapping his refined lead anodes in cotton fabric. The theory is that sulphuric acid collects in the interstices of this envelope, preventing access of ferrous iron through diffusion, when proper strength of current is applied so as to accelerate speed of cations toward the cathode as compared with their rapidity of diffusion. The thickness of wrapping is in inverse proportion to density of current.

Lead anodes cannot be used when the solution contains soluble chlorides, as the chlorine liberated through electrolysis attacks the metal. Much trouble arose from this source in lixiviating at Kakaralinsk, Russia, owing to impurities in the water used.

At the Butte-Duluth plant the lead anodes contain six percent antimony. They measure 24 in. by 38 in., and weigh about ten pounds per sq. foot. Anodes of this description are also used in electrolytic refining plants in treating solutions which have become too highly charged with iron, etc. No trouble is experienced unless chlorine is present. Lead removed from anodes through corrosion is not lost, but may be recovered from residues settling in the cells.

On account of rapid disintegration, carbon has been considered unsuitable as anode material in electrolyzing sulphate solutions. Recently, however, a combination of carbon and lead

* U. S. patent No. 757,817.

has been found to give satisfaction when sulphur dioxide is present in the electrolyte.

At the Chuquicamata plant fused magnetite is to be used for anodes. This material is said to be unaffected by oxygen, chlorine, or sulphur dioxide. Apart from their brittleness, these anodes appear to answer fairly well the purpose for which they are intended.

ELECTROLYSIS OF COPPER SULPHATE SOLUTIONS.

As deposition of copper from sulphate solutions is influenced by current density, dilution of electrolyte, nature of soluble salts present, amount of free acid in the bath, corrosion of the deposited metal, temperature, etc., it is manifest that the process is of complex nature. This may partially explain diverse opinions expressed by engineers relative to practicability of electrolysis in depositing metal from ore-lixivium. It is plain that if undesirable elements are removed from the electrolyte previous to electrolysis, and if the greatest quantity of copper attainable is introduced, results will be much better than when comparatively weak liquors, saturated with impurities, are treated. The literature on the subject is replete with descriptions of methods (and suggestions) for increasing copper content of weak lixiviums, and for removing deleterious elements. The use of reducing agents in a measure counteracts the bad effect of ferruginous salts; but size of plant is largely increased on account of low current density alone permissible under such conditions. It has been stated that the current density must be reduced to three amperes per sq. foot in order to get satisfactory deposition of copper.

One ampere of current passed through a copper sulphate solution should theoretically deposit very close to one ounce avd. of metallic copper in 24 hours. This would be 100 percent current efficiency, and although such results have been reported from small scale experiments, when using comparatively rich electrolyte and depolarizers, they can hardly be expected in commercial practice. There are many ways in which current is consumed in an electrolytic cell without causing permanent copper deposition. For instance, a warm electrolyte facilitates passage of the current, but also subjects the metal already deposited

to corrosion; and the well-known anodic oxidation of cations, with their subsequent reduction at the cathode, has been so often referred to as hardly to warrant further mention.

To render electrolysis of copper solutions practicable, ratio of capacity of plant to capital invested must be brought within definite limits. In other words, operations of this nature must be conducted at fairly high current densities. But high current densities, on account of the great ohmic resistance offered by average ore-lixiviums demand voltages which cause deposition of other elements. It therefore becomes at times important to separate copper salts from salts of metals reduceable under conditions which it is proposed to maintain in the cell, or to interpose means of rendering deleterious elements innocuous.

Although it is generally conceded that presence of considerable iron is objectionable in cupriferous solutions undergoing electrolysis, some difference of opinion has existed as to quantity of this metal which is distinctly harmful. Mr. N. V. Hybinette* states, that the disturbing influence of ferric salts on deposition of copper is negligible until there are present in the electrolyte more than ten grams ferric iron per litre, and that action of the ferric salt does not become serious before the amount has risen above 15 grams per liter. Rapidity of oxidation of ferrous iron depends on amount of that salt in the solution. Oxidation proceeds regularly as long as there is present not more than 30 grams per liter of ferrous iron, but ceases when content has fallen to 15 grams per liter of ferrous iron. Therefore, as long as there is not much more than 30 grams per liter of ferrous iron present, production of ferric sulphate to an objectionable degree takes place slowly, and, as stated, action on the cathode is not serious with concentration of ferric salts amounting to 15 grams per liter. The solution on entering the electrolytic cells contains about 2 to 5 grams per liter ferric iron, and leaves with about 15 grams per liter. The amount of iron held in the circulating solution is kept at the desired point by periodically discharging the necessary proportion.

Methods of removing iron from copper lixiviums by simply blowing air into them, or by treatment with calcium carbonate, have been repeatedly tried but have not proven satisfactory.

* U. S. patent No. 1,122,750, Dec. 29, 1914.

Ottaker Hofmann* gives a method of purifying copper sulphate solutions which frees them from the greater part of their contained iron, arsenic, antimony, and bismuth, while increasing the copper content. The lixivium is heated, and when hot, roasted matte is added and air is forced through the mixture. This method was tried by Hesse at Predazzo in southern Tyrol.† The lixivium treated was neutral and nearly saturated, assaying 40 grams per liter in copper, 0.8% to 1.1% ferrous iron, and 0.03% ferric. After removing what iron was practicable, it assayed 60 grams per liter in copper and 0.08% iron. In place of matte, Hesse used roasted concentrates.

At the Kalakent copper works in Russia‡ impure lixivium was passed over dead-roasted matte, and then over low-grade copper ore. The liquor was afterwards diluted, heated, and air was forced through it. Scrap copper was used to take up any excess acid remaining.

A method employed in electrolytic refining establishments to remove undesirable impurities from the electrolyte when it became overcharged with these, was to treat portions of the liquor in special cells. Lead anodes were used, and a voltage was maintained which sufficed for deposition of arsenic and antimony, but left the iron in solution. Iron was then separated as ferrous sulphate by crystallization. In ore-lixiviums, arsenic and antimony are seldom present in quantities sufficient to cause trouble.

Metallic deposition on the cathode is influenced by relative quantities of different ions in the electrolyte. As long as copper salts are present in proper proportion, other elements usually contained in sulphate ore-lixiviums are not apt to be deposited, but when the liquors become impoverished as to copper, then other ions serve to transport the current, and undesirable elements appear at the cathode. No current traverses an electrolyte unless conveyed by ions of some description. For this reason, when gravity circulation of electrolyte alone serves as means of replenishing the supply of copper ions where they are needed, electrolysis of copper sulphate solutions becomes unprofitable as soon as content of the electrolyte sinks to about one percent cop-

*"Hydrometallurgy of Silver".

†"Metallurgie", 1919, page 580.

‡"Modern Electrolytic Refining", by Titus Ulke.

per. Moving electrodes cause circulation of electrolyte and therefore assist in electrolyzing weak solutions.

Depolarizers commonly used in depositing copper from ore-lixivium are sulphur dioxide and ferrous iron. The theory of the action of depolarizers is, that they absorb oxygen liberated at the anode, thereby reducing voltage necessary for carrying on the operation by decreasing counter-electromotive-force. Ferrous iron by itself can be used in quantities sufficient to act as a depolarizer only when the cell is provided with a diaphragm; for when the iron is raised to the ferric state, disturbances are brought about which have already been mentioned. Depolarizers are said to preserve carbon anodes from disintegration.*

As it has been found undesirable to use diaphragms in electrolyzing copper sulphate solutions, and as ferrous iron is not available as a depolarizer without diaphragms unless the solution is saturated with sulphur dioxide, then sulphur dioxide must be considered as the essential in such operations, and ferrous iron as an auxiliary. Diaphragms are always to be avoided when possible. They are difficult to maintain so that solutions will not leak from one compartment to the other, and they increase ohmic resistance of the bath by interfering with passage of the ions.

Sulphur dioxide is itself subject to electrolysis, and undergoes decomposition at the cathode under certain conditions. When the electrolyte is impoverished of its copper ions, or voltage rises, elemental sulphur is released at the cathode, which, combining with nascent hydrogen, produces hydrogen sulphide. In this way copper has been precipitated as CuS from weak electrolyte.

When sulphur dioxide is used as a depolarizer in electrolyzing ferruginous copper sulphate solutions, the impressed voltage required to deposit copper is necessarily lowered, because of reduction of counter-electromotive-force. Under such conditions, drop of potential to as low as 0.6 volt has been found possible, and danger of deposition of iron is avoided.† Addicks‡ states that experience at Douglas (Arizona), when employing sulphur

* Compare C. J. Tossizza, U. S. patent No. 710,346, Sept. 30, 1902.

† C. J. Tossizza, U. S. patent 710,346, Sept. 30, 1902.

‡ Trans. A. I. M. E., Salt Lake meeting, 1914.

dioxide in electrolysis, was of similar nature, and that it is possible to consider working voltages as low as 0.6 to 0.7 volt. Of course there must be vigorous circulation of the electrolyte, or other means of bringing the gas into contact with the anode must be adopted, to render the sulphur dioxide effective.

Ore lixiviums (and electrolytes) are not good absorbers of sulphur dioxide gas under atmospheric pressure, and therefore some difficulty has been experienced in introducing this gas into such liquors. Reinartz‡ has given a method of trapping the gas under slight pressure, which, on a small scale, produced excellent results.

Sulphur dioxide gas is absorbed by ore-lixiviums when permitted to trickle down through absorption towers, and saturated liquors may be obtained in this way from roaster gases. Blowing roaster gases into vats, or electrolytic cells, filled with solution, is not so effective, as the gases escape in large bubbles. The coefficient of absorption for sulphur dioxide gas in water is greatly reduced by its dilution with air and furnace gases.

At Anaconda it was found that sulphur dioxide in roaster gases from a McDougall furnace containing ten percent SO_2 was readily absorbed by ore lixivium when forced in under 15 lb. pressure per sq. in. During the first hour, absorption of SO_2 was almost complete, and then gradually fell off to about 60%. The absorbing solution contained: Cu, 2%; NaCl, 8.5%; H_2SO_4, 0.5%.

A further advantage obtained from employing SO_2 as a depolarizer in electrolysis is the formation of H_2SO_4 in the cell. A distinction should be made between acid regenerated from lixivium and new acid formed out of SO_2. Theoretically, electrolytic decomposition of $CuSO_4$ sets free (regenerates) about 1.5 lb. H_2SO_4 for every pound of copper deposited, and an additional 1.5 lb. of H_2SO_4 is manufactured by combination of the oxygen liberated from copper sulphate at the anode with SO_2 present in the electrolyte. The more completely the SO_2 distributed throughout the liquor is brought into contact with anodic oxygen, the better the results. As some oxygen always escapes, anodic efficiency is usually low.

‡ "Metallurgie", 1908, page 202.

CURRENT CONDITIONS.

Copper is deposited in electrolytic cells in different form, according as the conditions vary under which deposition takes place. The metal may appear at the cathode in a firmly adhering mass, or it may be granular and loose, or even pulverulent, according as current density and concentration of salts in the electrolyte are altered. The most important point to consider relative to obtaining a good deposit of metal is keeping an adequate supply of copper ions in immediate vicinity of the cathode. Weak solutions will yield firm deposits of clean copper if this precaution is taken.

Current density permissible in carrying on electrolysis of copper sulphate solutions varies greatly with conditions in the cell. That metal is usually liberated at the cathode first, which combining to form a sulphate produces the least amount of heat. For this reason copper is deposited in advance of iron, provided current density is properly regulated and preponderance of ferruginous ions is not too great. High current density may deposit several metals simultaneously, and if the electrolyte is very acid, hydrogen is also liberated.

The current density generally employed in depositing copper from sulphate lixivium is low—eight to twenty amperes per sq. ft.—but current density as high as 45 amp. per sq. ft. has given a good deposit in the oscillating type of cell. Bennett reports a deposit "as good as the best" with 2400 amp. per sq. ft., using a rotary cathode.

At the Butte-Duluth plant, where electrolysis of sulphate solution has been in commercial operation for some time, current densities varying from eight to thirteen amp. per sq. ft. have been reported. At the Bullwhacker plant the current density used is said to have been 13 amp. per sq. ft., and Keith experimented with current densities ranging from 15 to 20 amp. per sq. ft. at the Arlington plant (New Jersey). The Intercolonial Copper Co. (Nova Scotia) is said to have used current density of 6 amp. per sq. ft.

It is evident from published statements that it has been found expedient to make use of comparatively low current densities (about 12 amp. per sq. ft. on the average) when electrolyzing

copper sulphate solutions with gravity circulation. When depolarizers are employed, under the same conditions, current density must be greatly reduced (3 to 6 amp. per sq. ft.). With moving electrodes, higher current densities are permissible in proportion to celerity of motion. It would, therefore, seem possible to construct electrolytic cells having much larger capacity per unit of electrode surface than those now in use. First cost of such a plant would be reduced as compared with existing ones, but energy required per pound copper deposited would be greater. Saving in time, and interest on investment and on material undergoing treatment, would be in favor of the smaller, rapidly-operating installation.

To effect decompositon of a metallic salt through the agency of the electric current, a certain minimum electromotive force is required, corresponding to amount of heat liberated when the metal under consideration combines to form said salt. In the case of cupric sulphate this force is about 1.2 volts. In addition to energy expended in releasing metal at the cathode, a further quantity is consumed in overcoming various resistances in all cells, and in doing certain work appertaining to electrolysis.

It has been found in practice that in electrolyzing a copper-sulphate ore-lixivium, about two volts pressure are required with the ordinary copper refiners cell. Keith used 1.6 volts per cell; but he had a high-grade solution (6% Cu); and the Intercolonial Copper Co. is said to use 1.5 volts, with a depolarizer. Bennett found that the voltage in his rotary cell increased with speed of revolution of the cathode. At 1750 revolutions per minute, a little over three volts were required: at 3500 revolutions the voltage had risen to nearly five. High voltage does not necessarily imply deposition of undesirable elements on the cathode, provided a sufficient supply of the more easily reduced compound is maintained.

If electrolysis is performed under favorable conditions, theoretical effect of current can be attained at the cathode—that is to say, current efficiency will be 100 percent. But in practical work the usual current efficiency is low. This is because current is expended in other ways than in depositing copper—liberation of hydrogen, reduction of ferric salts at the cathode, heating electrolyte, etc. In a series of experiments made at the Greenawalt

testing works in Denver, using a movable anode, current efficiencies attained ranged from 51 to 87 percent. At the Intercolonial Copper Co.'s plant 90-percent current efficiency was reported in reducing copper content of bath from 2.5 to one percent copper. At the Butte-Duluth works one pound of copper was said to be deposited per kilowatt-hour consumed. As drop in potential across the electrodes measured, on the average, two volts, current efficiency was about 76.5 percent. Laszczynski reported that with his apparatus one metric ton of copper was produced with an expenditure of 135 horsepower. This would be 0.912 lb. Cu per kw-hour. As the cell voltage was 2.5, this represents a current efficiency of about 87.2 percent. At Douglas, Addicks states that it is aimed to obtain a recovery of three pounds copper per kw-hr., employing from 0.6 to 0.7 volt pressure. At 0.65 volt this would mean a current efficiency of 74.6 percent.

Energy efficiency attained in electrolyzing copper sulphate lixiviums is generally much lower than corresponding current efficiency, unless a depolarizer is used: it is generally below fifty percent. The power required to deposit a given amount of copper from sulphate lixivium is six times, or more, that expended in producing cathode metal by ordinary electrolytic refining. Mr. Claude Vautin states that it is safe to calculate upon about 3.33 tons (three long tons) output of cathode copper per horsepower-year by the electric method of precipitation. Energy efficiency at Miedzianka (Poland), where Laszczynski's process was used, figures out at about 42 percent: at the Butte-Duluth plant at about 46 percent.

At one cent per kw-hour, the cost of power for electrolytic deposition is not excessive. The Butte-Duluth company is said to buy power for about $40.00 per horsepower year, which is equivalent to approximately $0.006 per kw-hour.

The power problem in electrolytic deposition of metals was discussed by Addicks and others at the January (1914) meeting of the New York section of the American Electrochemical Society.

ORE LEACHING VATS.

By far the greater part of the ore which is destined to be subjected to treatment by leaching processes will be low-grade

—probably less than two percent copper. To lixiviate a low-grade ore to best advantage, it must be handled in large quantities with minimum preparatory treatment. Percolation of comparatively coarsely crushed material in large vats meets these requirements. Rectangular reinforced-concrete vats which can be filled and discharged from the top by means of mechanical appliances afford the cheapest means for handling large quantities of material by leaching methods. Expensive apparatus for removal of leached tailing from vats may not always be warranted in works of small capacity, and in such cases circular vats, constructed either of reinforced-concrete or wood, may be employed. These are usually provided with openings in the bottom for discharging the tailing.

Concrete vats have long been used for leaching operations, when the solutions were weakly acid. As cements employed in mixing concrete contain free lime, this material is strongly alkaline, and therefore concrete is not well adapted to resist acid solutions. When the liquors are weakly acid, or nearly neutral, a protective coating of gypsum appears to form, and this in a measure preserves the concrete from rapid destruction.

Oil-impregnated mortar used in mixing concrete gives a very satisfactory material for constructing leaching vats. Because of inferior strength, such concrete must be more heavily reinforced than is necessary with plain concrete; but with solutions carrying as high as two percent H_2SO_4 it has shown itself to have satisfactory resisting qualities.

All attempts at covering concrete with acid-proof material, so far reported, have been disappointing. Tar, asphaltum, paraffine, patent paints, etc., when applied as coatings, have all proven unserviceable on exposure to strong (10%) acid liquors. The acid penetrates to the concrete backing through cracks or small holes, and soon loosens the protective lining.

When a vat is desired of large dimensions and strong acid-resisting qualities, probably the best that can be constructed is one of reinforced concrete lined with acid-resisting brick laid in asphaltum, and backed with hot asphalt poured between brick and concrete. Croasdale recommends pressed vitrified brick of uniform size, laid flat rather than on edge. As asphalt is apt to soften when exposed to moderate heat, and to become brittle and

crack when cold, under some circumstances laying the brick in oil-mixed cement mortar may be preferable to asphalt.

The bottoms of brick-lined concrete vats are satisfactorily made of sand and asphalt, pressed solid with a heavy iron muller. Brick paving may be laid on top of these bottoms. A new departure in the way of concrete ore-leaching vats is being tried on a very large scale at Chuquicamata (Chile). These vats are lined with mastic asphalt, specially prepared for the purpose. The ore capacity of each one of these vats will be about 10,000 tons.

Leaching vats used at the Gumeschevesky mine* were constructed of masonry and lined with four inches of concrete protected with one inch of asphaltum. This lining is said to have lasted two years exposed to a temperature ranging from 40° to 102° F. (4° to 39° C.). Croasdale observed that evaporation from concrete vats is less than from similar vessels constructed of iron.

Wooden vats are usually built round, and when constructed of some western woods have shown remarkable acid-resisting qualities.† It is said that eastern woods are less suitable, but others report that wooden vats have given quite satisfactory results in connection with electrolysis of copper solutions when no lead lining was used.

In the 80-ton experimental plant at Anaconda there were two redwood vats 32 ft. diameter and 12 ft. deep. Five discharge gates, each twelve inches in diameter, were placed in the bottom of each vat, and the tailing was sluiced out through these. The vats were also provided with filters constructed of 2-in. by 4-in. pieces, spaced one inch apart. Inch slats, also placed at one inch intervals, rested on the lower frame-work at right angles to the two by fours. The whole filter frame was nailed together with copper nails and made in sections for convenience in handling. On top of the frame two layers of coarse cocoa matting were placed. There was a lead lining under the filter and for six inches up the sides of the vat.

The tanks in which stock solutions were kept were also of redwood, but were lead-lined. They were slightly smaller than the leaching vats. Concentrated acid was stored in iron tanks.

* A. L. Simon, Bull. No. 65, Inst. of Mining and Metallurgy.

† Compare Eng. and Mg. Journal, Feb. 13, 1915, p. 315.

ten feet by ten feet, all connections and fittings were of iron. An old Oregon-fir vat, 28 feet diameter, answered as spare acid reservoir.

At the Butte-Duluth plant a circular wooden vat was tried for electrolyzing purposes. It is said to have given satisfaction although it had no lead lining.

The Mining & Scientific Press of March 7, 1914, contains an instructive article by Mr. J. M. Lillegren on "Assembling and Erecting Wooden Tanks".

Electrolytic cells have been constructed of wood and are usually lead lined: concrete has also been used for the purpose. When the electrolyte does not carry over two or three percent free acid, oil-mixed concrete is not seriously affected.

At Anaconda, wooden vats nine to ten feet in diameter, with agitator equipment, were used in precipitating copper by means of sponge iron. They were not lead-lined and did not leak. When NaCl was added to the liquors in two large lead-lined solution vats, they leaked. This is explained by generation of HCl through mixture of NaCl with H_2SO_4 and consequent action of the acid on the lead linings. As the wood backing was dry, the liquor found its way through.

MISCELLANEOUS APPARATUS.

In leaching operations it is necessary to frequently elevate corrosive liquors from one part of the mill to another, and for this purpose various appliances have been employed. Owing to the admirable apparatus now available, this problem no longer presents serious difficulties. In selecting pumps for use in handling cupriferous solutions, two factors have to be borne in mind: they must be able to withstand strong corrosive liquors, as well as abrasive action of mineral particles. It is a matter of record that in the past promising processes have been known to fail because of difficulty in obtaining pumps which could deal with strongly acid liquors of feculent consistency.

In recently constructed plants two types of solution-elevating apparatus have been successfully applied: centrifugal pumps, and air-lifts. The plunger type of pump is now rarely, if ever, employed.

Centrifugal pumps for use in copper hydrometallurgy are

now made either of stoneware or of metal. At the Butte-Duluth plant a stoneware centrifugal pump, manufactured by the German-American Stoneware Works, gave satisfaction. This pump was said to elevate 200 gallons per minute of strong acid lixiviant 40 feet vertically with an expenditure of four horsepower. In case of wear or breakage, new parts for such pumps are readily obtainable from the manufacturers at reasonable cost. All pipes and connections used with this pump were of lead, as sulphate solutions were being elevated. Lead, of course, is not suitable for use with a circulating system handling chloride solutions.

Hard-lead centrifugal pumps are also reported to have given satisfaction, but the stoneware apparatus appears to be the favorite. Some difficulty has been found with the lead centrifugals in keeping the packing tight without cracking the lead casing or stuffing gland, and wear on shaft is said to be excessive.

Air-lifts have been repeatedly recommended for circulating solutions of corrosive nature. Their suitability for the purpose is easy to understand, for, having no moving parts, if constructed of material capable of resisting corrosive and abrasive action of the liquors, they should last indefinitely—barring accidents. At Anaconda an air-lift was provided for each vat. Having a capacity of 250 gallons, or more, per minute, its function was to circulate the lixiviant by elevating it 16 feet vertically through a five-inch lead pipe. There was no appreciable corrosion at the elbows, where the greatest amount of wear would naturally be expected. The average specific gravity of the solutions was about 1.22, and they were more or less viscous. Occasionally the liquor foamed and caused trouble: cold solutions foamed worse than warm ones.

A Pohle air-lift pump, constructed mainly of wood, for use with very corrosive solutions, was described in a paper read by Mr. T. P. Holt at the Salt Lake meeting of the Am. Inst. of Mining Engineers, August, 1914. The Pohle air-lift pump is considered by some to be the most suitable apparatus for handling liquors met with in copper leaching. The air-lift used at Park City (Utah) elevated solutions 37 ft. vertically with an average of 27 lb. air pressure. Mr. R. H. Shaw, in the "Colorado School of Mines Magazine" (reproduced in Mining & Scientific Press, Nov. 29th, 1913,) has described another simple form of air-lift.

Wooden pipe, and wooden launders without lead lining, answer requirements where gravity flow of corrosive sulphate solutions is concerned. Sectional wooden pipe tied together by heavy wire, whether steel or copper, is apt to fail, because the solutions are certain to find egress through some defect in the joining, or in the material, in which case both of the metals mentioned are rapidly corroded. At Anaconda it was found that the lead in lead-lined launders would sometimes creep and split at the seams. Launders made of reinforced concrete have also been used for transferring solutions.

It is sometimes of advantage to heat solutions, and this may be accomplished by live or exhaust steam. If the steam is introduced into the liquors direct, it condenses, thereby causing dilution. To obviate this, it is passed through lead pipes. At Anaconda the corrosive action of solutions carrying from three to four percent free acid rapidly destroyed lead pipe used for this purpose. With solutions containing one percent acid, or less, no corrosion of the lead pipe was observed after several months continuous use. Lead-lined iron pipe is adapted to conveying corrosive sulphate solutions, especially where rigid pipe connections are necessary.

Pure rubber acid-proof hose resists corrosive action remarkably well. The initial cost is high, but its use is indispensable at top of vats.

Among metallic compounds capable of withstanding corrosive action, nothing so far reported equals "duriron". Unfortunately it is extremely brittle, and so hard that it cannot be machined. It resists to an extraordinary degree the most corrosive sulphate and chloride solutions.

DISCUSSION

Mr. Neal. **Mr. Walter Neal,*** Mem. Am. Inst. M. E., inquired regarding the use of sodium sulphate as a solvent for copper, particularly regarding whether it could replace sulphuric acid for this purpose.

Mr. Austin. **Mr. W. L. Austin,**** Mem. A. I. M. E., replied that he had not heard of sodium sulphate being used in the lixiviation of copper ores, except as an addition to the charge in roasting, with a view to sulphatizing the copper. As to other solvents, he mentioned that ferric sulphate and chloride had been tried.

* Salt Lake City, Utah.

** Riverside, Calif.

Prof. Clevenger.

Prof. G. H. Clevenger,† Mem. Am. Inst. M. E., stated that doubtless Mr. Neal meant sodium bisulphate rather than the sulphate.

Mr. Hamilton.

Mr. E. H. Hamilton,‡ Mem. Am. Inst. M. E., stated that the reason that sulphuric acid is so generally used as a solvent is on account of the fact that it can be readily replaced from the sulphur contained in the ore.

Mr. Duschak.

Mr. L. H. Duschak§ asked Mr. Austin whether he had heard of any recent developments in the preparation of hydrogen sulphide from sulphur and hydrogen. He stated that a report had come to him that this was being done at Well City, Missouri, in connection with the precipitation of copper from mine water. He further stated that this method of producing hydrogen sulphide had received very little attention, but it nevertheless seemed possible that a method of manufacture along these lines might be developed, similar to the contact process for making sulphuric acid.

Mr. Austin.

Mr. Austin replied that hydrogen sulphide can be produced so easily in other ways that he did not see the advantage of making it synthetically. He called attention to the fact that it can be generated from certain types of refuse.

Mr. Duschak.

Mr. Duschak inquired as to what kind of refuse he referred to.

Mr. Austin.

Mr. Austin replied that the hydrocarbon residues from oil works or the fats from slaughter houses can be treated with elemental sulphur to produce sulphuretted hydrogen. He also called attention to the fact that the gas can be cheaply produced by passing producer gas through a bed of heated pyrite.

Mr. Duschak.

Mr. Duschak asked if these methods would not be fairly expensive, since they would necessitate the shipping of a large quantity of material for the small quantity of hydrogen sulphide produced.

Mr. Austin.

Mr. Austin replied that he estimated that the hydrocarbons and sulphur could be shipped to comparatively distant points and hydrogen sulphide produced at a cost of about 2 cents per pound of copper precipitated.

Prof. Clevenger.

Prof. Clevenger asked Mr. Austin regarding the method of making hydrogen sulphide from oil refinings and slaughter house refuse and sulphur.

Mr. Austin.

Mr. Austin replied that the operation could be readily carried on in a retort and, upon a small scale, in a flask or wine bottle; in other words, all that is necessary is to bring the two materials, hydrocarbon waste and sulphur, together and heat the mixture, when hydrogen sulphide is evolved. He said that a low heat is employed and that the gas comes off very gently; whereas, if a higher temperature were used, evolution of the gas might become so rapid as to cause an explosion. He also called attention to the fact that, on a small scale, this method of making

† Stanford University, Calif.
‡ Smeltery, Trail, B. C., Canada.
§ San Francisco, Calif.

Mr. Austin. hydrogen sulphide is sometimes more convenient than the use of iron sulphide and an acid.

Prof. Clevenger. **Prof. Clevenger** stated that he hesitated to say anything upon the subject of the hydrometallurgy of copper in the presence of Messrs. Austin, Ricketts, Addicks and others who had carried on such extended investigations in this direction, but that he had to confess to being somewhat of an enthusiast upon the subject. He stated that he felt that hydrometallurgical treatment was perhaps going to solve some of the biggest problems in connection with the metallurgy of sulphide ores; that, for example, if a solvent could be found for copper which would act upon the copper minerals alone, leaving unaltered the large mass of sulphide iron minerals usually present in copper ores, the smelting process would have to give way to such a process in many localities on account of the difficulty with smelter smoke. He said that this was merely a suggestion and that perhaps the nearest approach to such a solvent of which we now know is the alkaline cyanides. Certain work which Prof. Clevenger has carried on in connection with the cyanidation of gold and silver ores has indicated that at least certain of the copper minerals are quite soluble in cyanide solutions. However, cyanide is an expensive salt and, unless most of the cyanide could be recovered during the precipitation of the copper, it could not be economically used as a solvent.

Mr. Hamilton. **Mr. Hamilton** stated that he did not understand what was to become of the sulphur.

Prof. Clevenger. **Prof. Clevenger** replied that, with this condition of working, the sulphur would remain unaltered in the residue.

Mr. Addicks. **Mr. Lawrence Addicks,*** Mem. Am. Inst. M. E., called attention to the possibility of treating a copper ore by flotation, roasting the flotation concentrate, making acid from the fume and using this acid in leaching the roasted ore. He stated that this operation could be carried on considerably cheaper than present smelting methods.

Another member also asked Mr. Austin regarding the use of a chloride solution in leaching of copper ores. He said that he was under the impression that it was not a success when tried a number of years ago. He thought the process a very pretty one and thought that the old difficulties may have been overcome.

Mr. Austin. **Mr. Austin** replied that he thought the situation as to leaching copper ores with chloride solutions was at the present time about the same as it was ten or fifteen years ago. He said the process was attractive, but that the difficulty seemed to be in connection with electrolyzing a chloride solution. The cupric chloride acts on the anode, corroding the metal, and apparently slight pressure on the diaphragm causes a leak. When the cupric chloride gets through, the operation is at a standstill.

* New York, N. Y.

Mr. Duschak.

Mr. Duschak called attention to some work which Professor S. W. Young of Stanford University has been doing upon the colloidal properties of mineral sulphides. He thought that while this was important primarily in the study of the genesis of ore deposits, it might at least be suggestive in connection with the hydrometallurgical treatment of copper ores. He stated that Professor Young had found that a solution of hydrogen sulphide acts as a dispersing agent for copper sulphide minerals; for example, a massive piece of chalcocite when placed in hydrogen sulphide solution passes over into a brown colloidal form, in which form it would lend itself very readily to solution by a suitable solvent. This behavior of copper sulphide minerals might also be used to separate them from the associated iron pyrites and other gangue material.

Paper No. 178

THE DEVELOPMENT OF ELECTROLYTIC COPPER REFINING.

By

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The rapid progress of electrolytic copper refining in the past twenty-five years has been due to several causes. While the possibilities of the electrolytic separation of metals had been understood in a general way, there was no suitable source of current until the dynamo was practically developed in the seventies. This, at the same time, made possible the development of the whole family of modern electrical industries and thereby created the demand for high conductivity copper, which can only be obtained from very restricted pure ores or by electrolysis.

If we say that electrolytic refining costs ½c a pound over fire refining and that copper sells for 15c a pound, it will take but a 3 1/3% gain in conductivity to pay for the refining, when electrical uses are involved. Further, it is quite impossible to make a clean separation of silver and gold from copper by fire methods, while the "values" in cathode copper run but a few cents a ton. Copper is nearly always associated with silver and gold and our ½c a pound increase in cost calls for but $10 a ton of either or both of these metals to justify electrolysis from this standpoint.

The first commercial experiments, in this country, in the electrolysis of copper were carried out at Phoenixville, Pa., in 1879, but the tonnage handled was negligible for several years, and we may take, say, 1884 as the starting point for the industry. The first great difficulty was in keeping the purity of the electrolyte within reasonable bounds; the early electrolytic copper was very irregular in quality, resulting in a market premium for "Lake" copper produced from the pure native ores of Michigan. About

this time bessemerizing of copper was accomplished, resulting in a high elimination of impurities from matte, owing to the strong oxidizing action of the converter, and the universal adoption of this process removed the last obstacle to the expansion of electrolytic refining.

How rapid this expansion has been is shown in the accompanying table. As a matter of interest, the tonnage refined by the series and by the multiple processes are shown separately, as in the early days there was strong rivalry between the processes.

Both processes have survived and given relatively pure bullion; there is little to choose between them. The multiple process, however, is much less sensitive to impurities and requires less skill in operation, and has been adopted by those later entering the refining business.

Pounds per Year Electrolytically Refined.

Year	Series	Multiple	Total
1884	0	0	0
1890	.....	.....	.....
1896	102,000,000	150,000,000	252,000,000
1902	146,000,000	412,000,000	558,000,000
1908	430,000,000	734,000,000	1,164,000,000
1914	642,000,000	936,000,000	1,578,000,000

Three distinct stages in the development of copper refining may be noted; that of early development; that of tonnage extension; and that of efficiency work. The first period ends with the development of mechanical ladling, general use of cranes for handling electrodes and the undertaking of the building of the Raritan Copper Works in 1898. The second period covers the next half-dozen years, which saw the creation of the first really large plants; and the third, the ten years just closed, with plenty of work yet in sight to put refining on a finished basis.

Refining proper may be considered to begin with the treatment of copper bullion of the grade of converter blister and may be divided into anode furnaces, electrolysis—including production of power, electrolyzing, purification of electrolyte, and refining of anode slimes—and refining furnaces for the cathode product.

The anode and cathode furnaces have so many points in common that they may be considered together, taking the latter as the example. The size of charge taken out in the 24-hour cycle has steadily increased with the capacity of the plants, until it has become evident that the only practical limit is the tonnage a plant can supply. Before mechanical ladling was introduced, the size was limited to the amount that could be taken out by hand. Even when a bull ladle was used, 40,000 lbs. was considered a large charge. As soon as the Walker Wheel and other machines for mechanical ladling were successfully introduced, the size of charge was increased to 100,000 lbs., with marked lowering in all items of cost; and since then there has been a regular speeding up in each of the time-consuming elements making up the 24 hours, until with the modern charge of 600,000 lbs., or more, the refining is done for less than half the cost in the best of the old hand-ladled furnaces.

Furnace refining may be divided into charging, melting, rabbling, skimming, coking, poling, ladling and fettling. Charging is now done mechanically, by special cranes, at the rate of 300,000 lbs. an hour. Melting has been accelerated by means of forced and induced draft, the modern method being a combination of both in connection with waste-heat boilers. Mechanical stoking has been tried several times, as well as the use of fuel oil and pulverized coal. Up to this writing, however, hand-firing, combined with what is practically a gas-producer fire-box, has held its own. The coal consumption has fallen, with the increasing size of charge, from about 20% at 40,000 lbs. to 10% at 600,000 lbs. The fuel item is much smaller than in the case of either reverberatory matte smelting or open-hearth steel practice. Rabbling by hand has given place to blowing with compressed air. This, in turn, has raised structural questions in the design of the furnace on account of the consequent damage to the roof from the splashing of more or less oxidized copper. In anode practice this is now being met by the use of basic or neutral brick in the roof, and when melting cathodes, the blowing has been greatly curtailed. Skimming is still done by rabbles, but the proportion of slag made has been gradually reduced from 4% to less than 1% by keeping silica from the furnace lining, or from coal ashes, away from the cuprous oxide formed while melting and blowing.

Coking used to consist in blanketing the bath with charcoal, but crushed low-sulphur coke or anthracite has been largely substituted. Poling is still done with green hard-wood poles forced under the surface of the bath. Fuel oil has been tried, but it is difficult to avoid overpoling, on account of the rapidity of the action, and the sulphur content spoils the set of wirebar copper. Some hydrocarbon gas may be substituted in time. Ladling is now done mechanically at as high a rate as 90,000 lbs. an hour with one ladle and 120,000 lbs. an hour with twin ladles. This speed could easily be increased by tapping the furnace at two places. Fettling is practically eliminated with basic furnaces.

It is now realized that the only obstacle to changing the furnace refining of cathode copper into a simple melting is sulphur brought over as sulphates from the tank-house or absorbed from the products of combustion, etc., in the furnace. With a perfect cathode and a sulphur-free atmosphere, the process could be made a continuous melting, and steady progress is now being made toward this goal. The great capacity of modern furnaces is due partly to increased hearth area, but quite as much to deeper baths and the constant feeding in of fresh cathodes (or anode scrap) during poling and pouring. In some plants blowing has been practically eliminated, and the production of slag almost suppressed in the cathode furnaces.

Structurally, the main improvements in recent years have been along the line of substitution of magnesite and chrome brick for silicious material. Magnesite hearths are now thoroughly proved out for treating foul pig. Magnesite flash-walls, for all classes of work, are now yielding place to solid chrome walls, and chrome brick is contesting with silica brick in roof construction.

Turning now to the electrolytic part of the plant, we may dismiss the power problem very briefly as not being truly metallurgical in its nature. The characteristics of the power requirements are high amperage, low voltage direct current, with a 100% load factor. As individual circuits are limited to about 1500 kw., the reciprocating steam engine is at its best under these conditions, and up to date a high-economy, slow-speed, compound- or triple-expansion engine, generating a kilowatt-hour for about 15 lbs. of steam at 150 lbs. pressure sq. in., 100° F. superheat, and 27-inch vacuum, has been favored. The plants around New

York Harbor are able to procure steam sizes of anthracite at a much lower price than coal suitable for gas producer work. Considerable steam is also produced by the waste-heat boilers on the reverberatories. Gas engines have therefore been handicapped and have not as yet found a single application. The total capacity of the power plant has been a little too small, in extensions to existing plants, to justify the consideration of a central turbo-alternator of the great capacity necessary to develop a sufficiently low economy to offset the conversion losses in motor generators, and large high-speed direct-current turbo-generators are still in their infancy. We may therefore say that reciprocating engines still hold the field but that the indications are that the time is coming when they will have to surrender to a prime mover which can operate through a wider temperature range.

In the tank-house, capacity has been pushed from all sides. The Walker system of connections, whereby many tanks are placed edge to edge with but a small equalizing bar for carrying the current from the cathodes of one tank to the anodes of its neighbor, has been universally adopted, resulting in an increased efficiency in the use of floor space as well as cutting down the bus-bar investment. The size of the anode has been steadily increased, until several plants use electrodes three feet square, and in at least one leaching plant, four feet square. The number of anodes per tank has also been increased. Thirty-two have been successfully placed in space originally planned for twenty-six, and longer tanks can easily be used, the limit really being the amperage on the circuit. Current densities have gradually risen with the lower costs of power, until Eastern practice is close to 20 amperes per square foot. A current efficiency of about 90% seems to express the economical balance between labor and power. Lead-lined wooden tanks are still universally used in multiple-system practice, but their maintenance is a large item and much experimenting is now under way with various types of tank construction. The ideal system would be a large acid-proof basin without watertight division into single cells, the electrodes being supported independently by an independent bridge structure. Chemically, it is generally realized that a highly refined anode is more important than a pure electrolyte, and with anode copper 99% or over, an electrolyte with 2.5 to 3.0%

copper and 12% free sulphuric acid will give good results with almost any quantity of arsenic, nickel, etc. A good quality of anode has diminished the silver and gold losses in the cathodes until they are now but a small item—perhaps half of one percent of the anode contents at ordinary current densities. Basic anode-furnaces have made possible the production of a first-class anode from very foul raw material.

The general improvement in the grade of anode has simplified the problem of purification of electrolyte. The complete plan now used is to divert the necessary portion of electrolyte daily, remove the copper and arsenic as a cathode sludge, using insoluble anodes, concentrate the resulting liquor, first by steam in lead-lined tanks and then by direct heat in iron vessels, to a heavy liquor consisting of strong sulphuric acid and sodium sulphate, the sulphates of iron, nickel, etc., having fallen out as anhydrous salts. The sodium sulphate can be largely removed by chilling, if it is present in troublesome quantity, and the sulphuric acid returned to the electrolyte. The anhydrous salts form a starting point for nickel recovery. A small quantity of either hydrochloric acid or salt is added to the electrolyte, with the result that the antimony largely slimes as oxychloride. Glue or similar organic addition agents are generally used in very small quantity and greatly assist in forming smooth cathodes, although a slight excess greatly increases the working voltage. In general, six to seven pounds of cathode copper are obtained per kilowatt-hour.

The refining of the anode slimes is still in a transitional stage. A great deal of experimental work is being done on wet processes, on account of the metal losses associated with fire methods. As anode slimes are worth five to ten dollars a pound and a large refinery produces a couple of tons of such slimes daily, a considerable expenditure on treatment is permissible. A simple fusion of raw slimes will yield three superimposed molten layers,—bullion, matte and slag. The bullion is chiefly made up of the precious metals, lead and copper; the matte of copper, silver, selenium and tellurium; and the slag of the more easily oxidized elements, such as arsenic and antimony. The general plan in common use is to give the slimes a light roast to oxidize the copper, which is then dissolved as sulphate in suitable tanks.

The copper-free slimes form but little matte when smelted. After fusion in a small basic reverberatory the bath is skimmed clean and the base bullion refined to a high grade, done by blowing and nitreing. The slag is sorted, part sent back to the anode furnaces, part desilverized by a quiet fusion to free it from prills and part charged back into the silver furnace. The silver and gold are generally parted electrolytically and the resulting gold slimes treated for recovery of platinum and palladium. Selenium is recovered from the silver refinery flue dusts by leaching and reduction with sulphur dioxide.

One of the great difficulties in the way of devising a comprehensive wet process lies in the great variation in composition of the slimes at different times and places and in the number of elements present. The strong solvent action of ferric sulphate upon copper and the purity of silver chloride precipitated from foul solutions give a foundation for a wet process. The progress in electrostatic fume recovery is helping out the older process, however.

DISCUSSION

Prof. Clevenger. **Prof. G. H. Clevenger,*** Mem. Am. Inst. M. E., asked Mr. Addicks what the relative current efficiency is in the multiple and series systems of electrolytic copper refining.

Mr. Addicks. **Mr. Lawrence Addicks,†** Mem. Am. Inst. M. E., replied that the current efficiency is about 75% to 80% in the series system and 90% in the multiple.

Prof. Clevenger. **Prof. Clevenger** remarked that, of course, the lower current efficiency in the series system is due to leakage of current around the plates.

Mr. Addicks. **Mr. Addicks** replied that it is partly due to the fact that the anode and cathode are the same plate, so that a certain part of the copper may at times be deposited twice.

Prof. Clevenger. **Prof. Clevenger** asked how the circulation of the electrolyte is effected when the plates are placed close to the bottom of the tanks.

Mr. Addicks. **Mr. Addicks** replied that the circulation is very slow or otherwise the disadvantage would be encountered of stirring up the slime.

* Stanford University, Calif.

† New York, N. Y.

Paper No. 179

ELECTROLYTIC REFINED COPPER.

By

A. C. CLARK, Mem. A. I. M. E.
Raritan Copper Works
Perth Amboy, N. J., U. S. A.

Commercial electrolytic copper refining did not come into use until about 1860, and then batteries were used as a source of electric current for carrying on the electrolysis. The self-excited electric dynamo did not come into existence until 1866, and up to this date there was no demand for copper of high electrical conductivity, for the simple reason that the electrical era started about 1876, when the telephone was invented, followed during the next decade by the incandescent lamp, the arc lamp, and the electric railroad.

The Welsh process had been developed to a high state of perfection for the refining of copper by furnace methods, and whilst producing copper with satisfactory physical properties, it failed to produce a metal that was satisfactory for electrical uses, many brands of copper having a conductivity of less than 90%.

It is needless to add that the silver and gold could not be satisfactorily parted from the copper by the fire method, and thus about 1883 we find the question of electrolytic refining being widely considered as a means of copper refining; and in 1887 at least two small refineries had been established in the United States, producing between 8000 and 9000 tons of electrolytic refined copper per year.

From this beginning, the production of electrolytically-refined copper has gradually and steadily increased, until today in the United States we have the enormous annual output of

some 1,500,000,000 lbs. The source of this production is approximately as shown in the following table, which gives the monthly capacities of the several refineries, amounting to 140,000,000 lbs. per month or 1,680,000,000 lbs. per year, and which shows an excess capacity over actual production of 180,000,000 lbs.:

Raritan Copper Works, Perth Amboy, N. J.	33,500,000 lbs.
Nichols Copper Co., Laurel Hill, N. Y.	30,000,000 "
Baltimore Copper Smelting & Rolling Co., Baltimore, Md.	28,000,000 "
United States Metals Refining Co., Chrome, N. J.	18,000,000 "
American Smelting & Refining Co., Perth Amboy, N. J.	15,000,000 "
Anaconda Copper Mining Co., Great Falls, Mont.	5,000,000 "
Balbach Smelting & Refining Co., Newark, N. J.	4,000,000 "
Calumet & Hecla Mining Co., Hubbel, Mich.	4,000,000 "
Tacoma Smelting & Refining Co., Tacoma, Wash.	2,500,000 "
Total per month	140,000,000 lbs.

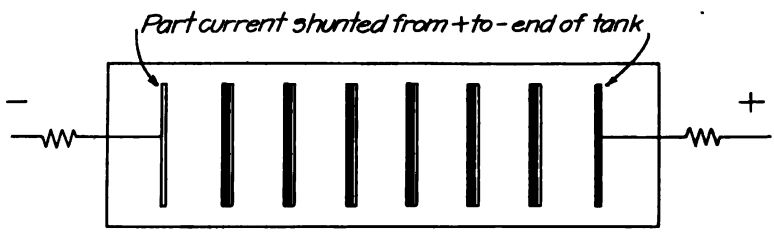

Fig. 1. Series System.

In addition to the plants named, several others have been operated in the earlier stages of the industry, among them being the large refinery of the Anaconda Copper Mining Company, located at Anaconda, Mont., and that of the New England Electrolytic Copper Company, at Central Falls, R. I. Both of these plants were, however, shut down some years ago, the latter plant, which was erected by Lewisohn Brothers, being closed when they established the Raritan Copper Works at Perth Amboy, N. J.

It may be of interest to note the order in which the various refineries commenced operations, and this is shown in the following table:

Refinery	Year	System Used
Balbach Smelting & Refining Co.	1883	Multiple
Baltimore Copper Smelting & Rolling Co.	1887	Series (rolled anode) and multiple
New England Electrolytic Copper Co.	1891	Multiple
Anaconda Copper Mining Co., Anaconda, Mont.	1891	"
Boston & Montana, Great Falls, Mont.	1892	"
Nichols Copper Co.	1893	Series(cast anode)
American Smelting & Refining Co.	1895	Multiple-Walker
Raritan Copper Works	1899	" "
United States Metals Refining Co.	1901	" "
Tacoma Smelting & Refining Co.	1904	" "

Speaking generally, there are two systems in use—the multiple and the series—each system being attended with its respective advantages and disadvantages.

The sketch (Fig. 1) shows the arrangement of the series system, where the copper to be refined is termed "bi-polar electrodes", each electrode being dissolved from one face in the process of refining, and the refined deposit of copper formed on the face opposite of the next electrode. This process probably found favor in the early days owing to the lack of a suitable generator—due to the fact that standard generators having a normal ampere output were satisfactory for use in the series system, while it was necessary to use a number of generators connected in parallel to generate sufficient ampere current for the multiple system. For instance, in 1893, the New England Electrolytic Copper Co. of the Lewisohn Brothers had a number of small generators running in parallel driven from a countershaft, with all the attendant difficulties of poor engine and voltage regulation, belt slippage, etc. The series system is still largely used, but the proportion of copper refined by this method is considerably less than formerly and all the later plants have adopted the multiple system.

The multiple system has been so greatly improved in recent years that at this time it represents a most satisfactory system of electrolytic refining. One of the principal difficulties formerly experienced with the multiple system was the complicated and expensive system of electrical conductors necessary to carry the current through the tanks. This has been largely simplified by

Arthur L. Walker, who has invented a system as shown in Figure 2. Instead of using one tank subdivided into two cells, with heavy copper bus-bars on each side of tank and individual connecting contact strips between the electrodes of each cell, Mr. Walker groups his cells in batteries of from 10 to 17, requiring only one heavy bus-bar for the first and last cells, and by using small triangular copper bars on the intervening partitions of cells, he effects a two-fold saving in voltage, due to a shorter electrical circuit and to a lower resistance due to the sharp contact between the anodes and cathode rods and the triangular bars. This system also largely decreases the cost of installation.

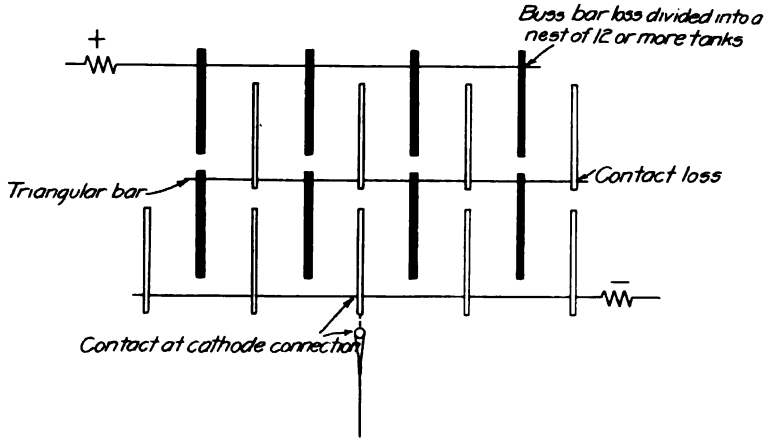

Fig. 2. Walker Multiple System.

The internal electric circuits,—namely the rod supporting the cathode and the clips between the cathode and cathode rod, the copper resistance of the anode itself, and the three electrode contacts—still form a serious loss in the multiple system that is not in evidence at all in the series system. However, the potential of the multiple system is so extremely low that it is easy to obtain an ampere efficiency of 90%, while with the series system the current leaking from the first positive to the last negative electrode in the tank effects a power loss which fully equals the loss by the voltage drop in the copper circuit and contact resistance of the multiple system.

Since the inception of electrolytic copper refining, a great

improvement has been effected in the quality of the refined product.

When electrolytic copper was first put on the market, it was irregular in quality, due to the presence of impurities, and consequently sold at a small discount from the price of Lake copper; and this discrimination in price has continued until the present day, but without any justification, for, owing to improvement in methods in operation, electrolytic copper is now uniform in quality, and when compared with Lake, is superior by analysis.

In the past, it was a common occurrence for the copper in the tanks to deposit itself in a soft and spongy condition and containing, in many cases, an excessive amount of arsenic, antimony and other impurities. In such cases the cathodes would be at once removed from the tanks and new cathodes started; and thus, from time to time, the quality of the refined product would vary, which resulted in an un-uniform quality wire bar or other casting.

This irregularity was due to a number of reasons, among which may be mentioned engine or generator troubles causing interruption of the flow of electric current, insufficient circulation of the electrolyte, undue variations in temperature, failure to maintain the solution in proper chemical proportion, etc., any one of which might produce an impure cathode copper.

Now, however, this is all changed, and by the development of the art and improved apparatus the modern refinery turns out a product absolutely uniform in quality, the cathodes being hard and smooth and assaying 99.96% copper.

As an illustration of the high degree of purity of electrolytic copper now produced, as compared to the earlier product, it should be noted that Matthiessen, in about 1865, established the maximum electrical conductivity of supposedly pure copper. On his basis, cathode copper now frequently shows a conductivity of 102.00% and over.

Arsenic is undoubtedly the most deleterious element which may be present in electrolytic copper, and the presence of very small quantities will very materially reduce the electrical conductivity. For instance, if 0.01% is present in the metallic form, the conductivity will be reduced approximately 3%. Conse-

quently, the greatest care must be exercised in the tank-room operations and in the subsequent furnace treatment to limit the arsenic contents to an exceedingly minute figure, the maximum percent permissible in first-class electrolytic castings being 0.002%, and this must be present in the oxide form. Figure 3

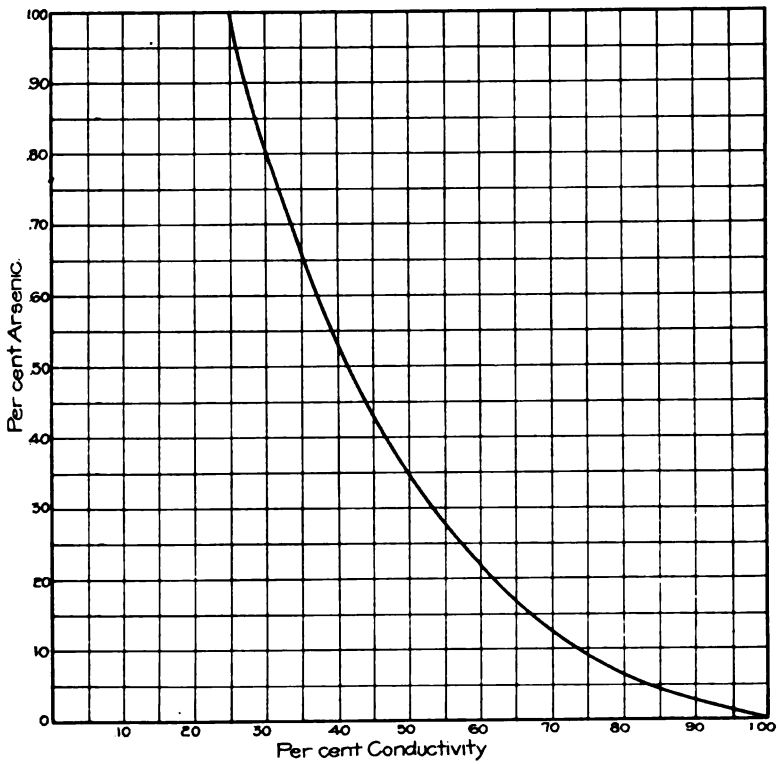

Fig. 3. Approximate Curve Showing Effect of Arsenic on Conductivity of Copper.

gives a curve showing the effect of arsenic on the conductivity of copper.

While the specifications of the wire mills have become more exacting, from time to time, in their requirements for physical and metallurgical properties, the refineries, at present, are able to produce castings which are entirely acceptable to the trade. Castings must conform closely to fixed dimensions and weights, must be reasonably free from cold shuts, fins and mechanical im-

perfections in general, and possess the necessary high conductivity. These conditions are met and, in fact, the electrical conductivity and physical properties exceed by a considerable margin the specifications called for by the American Society for Testing Materials for standard electrolytic copper.

Many improvements have been effected, in recent years, in the various departments of electrolytic refining. A special type of generator with extremely flexible electrical characteristics has been developed.

Solutions are generally circulated by means of centrifugal pumps invented by F. L. Antisell of Perth Amboy, this type of pump being used in most of the large copper refineries. It is constructed of hard lead, without packing glands or any wearing parts being subjected to corrosion of the solution and operates at a high mechanical efficiency with very little repairs.

Anode and cathode furnaces have been increased in size from a capacity of 50,000 lbs. and less to 500,000 lbs. and over per charge. Instead of charging by hand, charging machines (Ladd and Prosser patent) are used, which greatly increase the rapidity of the furnace cycle, effect a large saving in the cost of operations and render possible furnaces of large tonnage.

Furnaces are generally partially or wholly lined with magnesite or chrome brick, instead of the old silica-brick linings, thus effecting a saving in slag production and reducing the cost of repairs due to the corrosion of the furnace.

Owing to the increase in the size of furnaces, it became necessary to remove the molten copper more rapidly than could be done by the old hand-ladling method, and the McCoy and Walker casting machines were evolved and are now largely used. At the plant of the Raritan Copper Works, Perth Amboy, the Clark and Clark casting wheel was developed and is now in successful use on their 500,000-lb. furnaces. The copper is tapped from the furnace into the ladle and six bars poured at one and the same time, the moulds being set radially on the casting wheel. By this method, 100,000 lb. and over of standard-size wire bars are cast per hour.

Furnaces now are almost invariably equipped with waste-heat boilers of various types, and the result is a largely increased efficiency of the fuel used.

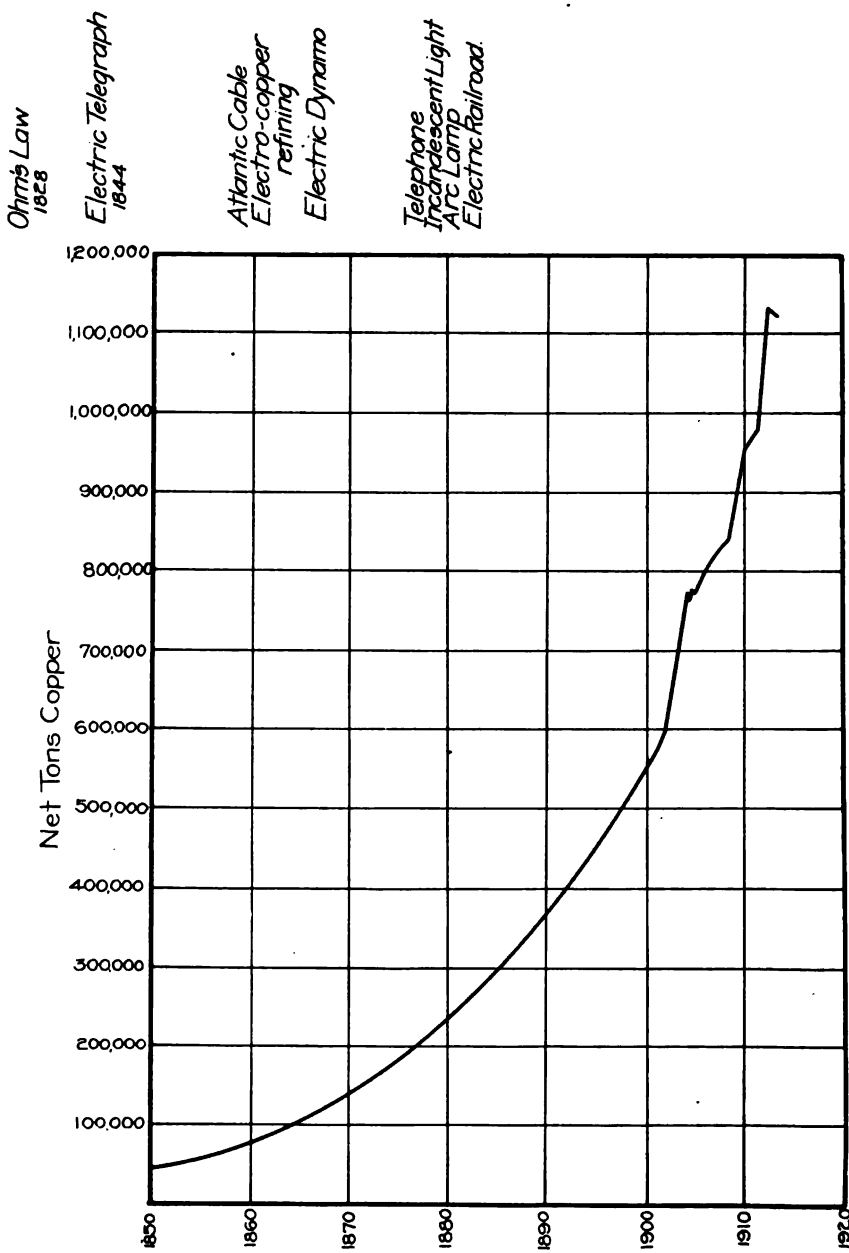

Fig. 4. World's Production of Copper from 1850 to 1913.

From the rapid increase in the world's production of copper, and considering the large proportion that is refined electrolytically, it is reasonable to suppose that considerable expansion may be looked for in the near future in electrolytic refining; and of the many new ore deposits now being developed, doubtless a large proportion will be treated electrolytically.

The curve in Fig. 4 shows the world's production of copper from 1850 to 1913. This curve may be of interest, as it indicates the rapid increase in the production of the metal. Of the production of 1,120,000 tons in 1913, about 68%, or 750,000 tons, was treated electrolytically in the United States; and of this amount, about 72%, or some 543,000 tons, was refined within a radius of twenty-five miles of Perth Amboy, New Jersey.

Paper No. 180

PHYSICAL PROPERTIES OF COPPER.

By

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INTRODUCTION.

The industrial uses to which a metal may be put are governed largely by its physical properties, although the question of expense usually determines whether the particular metal best suited for a given purpose is utilized.

The multitude of purposes for which copper is used to-day is due to both the above considerations. Improvements in methods of extracting the metal from its ores have made it available in large quantities at a comparatively low cost, while its physical properties make it ideal for some purposes and highly desirable for others.

In prehistoric times copper was used for simple cooking utensils and implements of war probably because it could be obtained easily and its ductility made it possible to form it into useful articles even with the crude methods then in use. Much of the metal used was not pure but was alloyed with other elements, which imparted desirable properties for some purposes and undesirable for others. It is probably true that the so-called tempered copper of the ancients was in reality a bronze which had been hardened by hammering.

As civilization spread and grew, the uses for copper multiplied and various elements were purposely alloyed with it to produce desirable qualities, but only recently has a systematic effort been made to study the effect of various impurities on the properties of copper and the effect of mechanical work and heat treatment on the metal and its alloys.

The results of much careful and systematic research along these lines on the part of great corporations producing or consuming copper and its alloys have not been published and are unavailable for public use, but, on the other hand, the results of research at various educational institutions and some industrial plants have been published and have proved of great practical importance.

It is the purpose of this paper to discuss the physical properties of copper in the light which has been shed upon them by numerous investigators, to whom the public owes a large debt for their painstaking work.

PURE COPPER.

Traces of oxygen are purposely left even in the highest grades of copper, so, strictly speaking, chemically pure copper has no general industrial use. Practically, however, the best qualities of tough-pitch-copper are usually spoken of as pure.

The melting point of copper has been fixed, by the latest investigators, as 1083° C. instead of 1084°, which was for a long time considered to be the correct temperature. The specific gravity of the solid metal is given by the Bureau of Standards as 8.89 at 20° C. This figure is lowered when the metal contains oxygen. The latent heat of fusion is 43.3 cal., and Kahlbaum has fixed the boiling point at 2310° C. The specific heat at 170° C. is 0.09244; at 100°, 0.09422; and at 300°, 0.09846. The coefficient of linear expansion is 0.000017.

Electrical Conductivity.

The use of copper for electrical purposes is so general that high conductivity is of importance in a large part of the metal produced. High purity is the first requirement, for even traces of an element which remains dissolved in the solid copper greatly lower the conductivity. Substances which do not remain dissolved in the solid copper are not so harmful, but yet lower the conductivity somewhat.

The ideal condition would be chemically pure metal free from pores, but this can only be approached, for it has been found practically impossible to cast a sound ingot of pure copper. If all the oxygen is removed from otherwise pure

copper, in the refining process, the metal readily absorbs gases, some of which are expelled during solidification, leaving the ingot porous and worthless for drawing into wire. It therefore becomes necessary, as previously stated, to leave traces of oxygen in the refined copper. This exists in the form of Cu_2O undissolved in the solid copper, and although less harmful than if it existed as a solid solution, its effect is noticeable.

Even the best of castings are somewhat porous and, therefore, relatively low in conductivity. Mechanical work on cop-

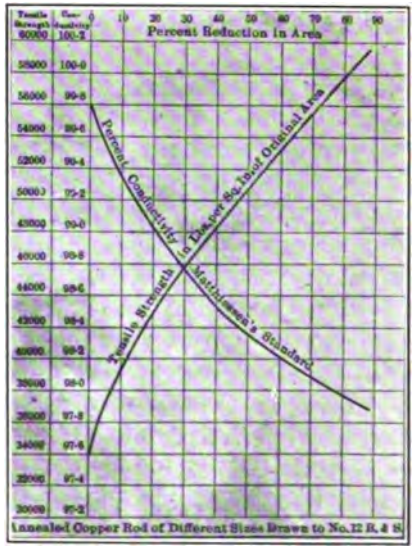


Fig. 1. Electric Conductivity as Affected by Mechanical Treatment (Addicks).

per greatly improves it in this respect; therefore, forgings rather than castings have usually been used for heavy conducting parts of electrical machines. Because of the lower cost of castings, many attempts have been made to so improve their conductivity that they could be substituted for forgings. Weintraub (Metal Industry, 1912, 10, 462) has succeeded in producing castings having a conductivity of 97 by adding small amounts of boron, carrying traces of oxygen, to the ladle just before casting. By this method the copper is deoxidized, but the casting becomes solid before gases can be absorbed to make

it porous. The boron and its oxide are insoluble in copper and thus lower its conductivity only slightly. The mechanical properties of castings produced in the above manner are excellent

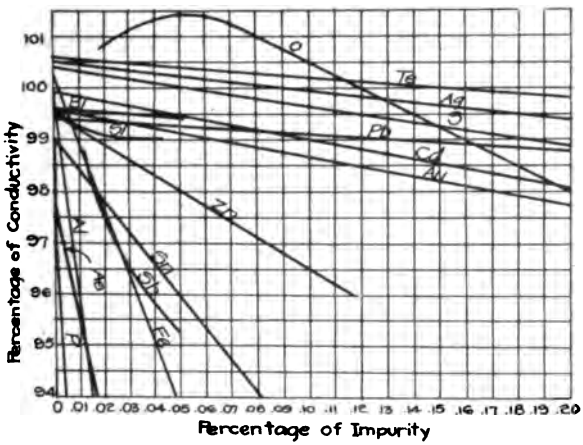


Fig. 2. Electric Conductivity of Copper as Affected by Impurities.

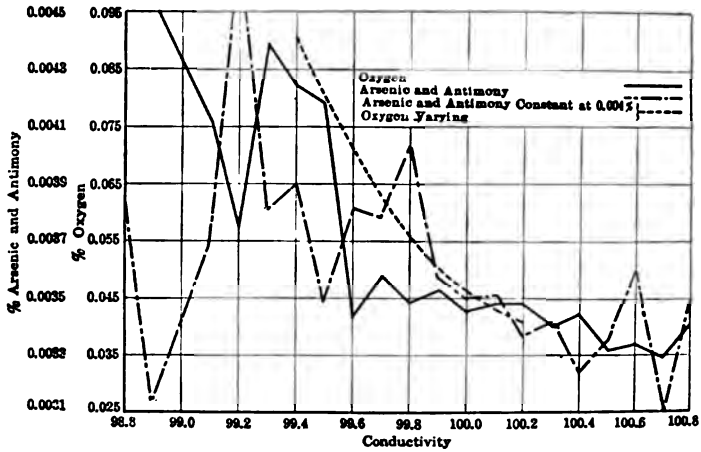


Fig. 3. Electric Conductivity of Copper as Affected by Oxygen, Arsenic and Antimony, Severally and Combined.

and they are being used in many cases as substitutes for intricate and expensive forgings.

Hard-drawn copper has a lower conductivity than annealed copper, but for mechanical reasons it is often necessary to use

the former. It can be readily seen that bending or twisting a wire will lower its conductivity, as it has the same effect on the metal as does mechanical work. In some cases, however, the apparent lowering in conductivity which has been noticed under these circumstances has been due to a reduction in the cross section of the wire.

Fig. 1 shows the effect of mechanical work on conductivity, and Figs. 2 and 3 the effects of various impurities. (Hofman, Metallurgy of Copper.)

Thermal Conductivity.

The thermal conductivity of copper is high in comparison with that of most metals, which makes it desirable for many purposes where rapid transmission of heat is an important factor. Its temperature coefficient is about 2½ times that of iron.

Widely varying coefficients for copper appear in the literature, which has led to an investigation by the Bureau of Standards. (Bulletin, Vol. 7, No. 1.) The results of these tests show that the thermal conductivity of copper varies uniformly with the electrical conductivity. The constant factor was found to be 0.00394. The electrical conductivity, expressed decimally, multiplied by this factor gives the temperature coefficient at 20° C.

This factor is of importance, as it may be used in calculating the electrical conductivity when the temperature coefficient is more easily obtained, as in the case of irregular specimens.

Experiments with wire wound around drums, twisted or bent, showed that the temperature coefficient was unchanged by this treatment.

Mechanical Properties.

The mechanical properties of copper depend on its purity and on whether it is cast, annealed, or had mechanical work done on it, in other words, on its physical condition.

The microscopic examination of polished sections has been valuable in studying the structure of copper electrodes, castings, forgings, etc., and much information has been obtained in this manner.

The structure of cathode copper has been shown by Faust (Zeit. Anorg. Chemie, 1912, 78, 201) to be crystalline, the size of the crystals varying inversely with the current density and directly with the concentration of the electrolyte. The first layer deposited consists of numerous small crystals, the growth of which is independent of the surface conditions of cathode

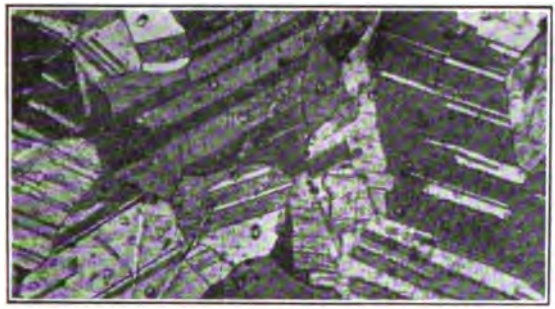
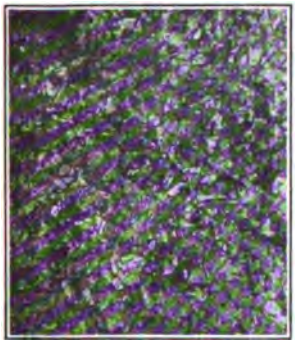


Fig. 4. Cathode Copper Heated in Vacuum One Hour (Faust).



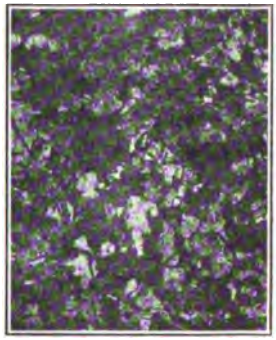


Fig. 5 (left). Rolled Copper.
Fig. 6 (right). Same as Fig. 5; Heated 40 Minutes at 650°-700° C.

and is parallel to the direction of the current. Not all of the small original crystals continue to grow. On annealing the cathode the crystals re-arrange themselves (Fig. 4).

The crystalline growth which takes place when electrolytic copper has been fused, cast, and rolled and subsequently annealed is shown in Figs. 5 to 9 (Faust).

The mechanical properties of copper at temperatures up to 900° F. have been studied by Huntington (Journ. Inst. Metals 1912, 2, 126), and his curves, which are self-explanatory, are shown in Figs. 10-13. The arsenical copper contained 0.234 As. The effect of annealing hard-drawn copper at different temperatures is shown in Fig. 14 (Hofman, "Metallurgy of Copper").

Fig. 7 (left). Same as Fig. 6; Heated 20 Minutes at 800° C.
Fig. 8 (right). Same as Fig. 7; Heated 10 Seconds at 900° C.

Fig. 9. Same as Fig. 8; Heated 20 Minutes at 1050° C.

Copper is mechanically improved by hot-working. It is closer grained than when cast and its strength and ductility are both increased. If, however, the working is continued when the metal is too cool to allow molecular re-arrangement, permanent distortion of the grains takes place, necessitating a subsequent annealing. Fig. 15 shows the so-called "slip bands" which occur when copper is rolled.

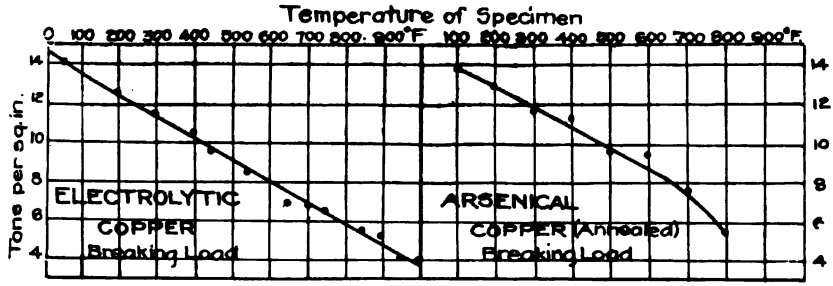


Fig. 10. Strength of Hot Copper.

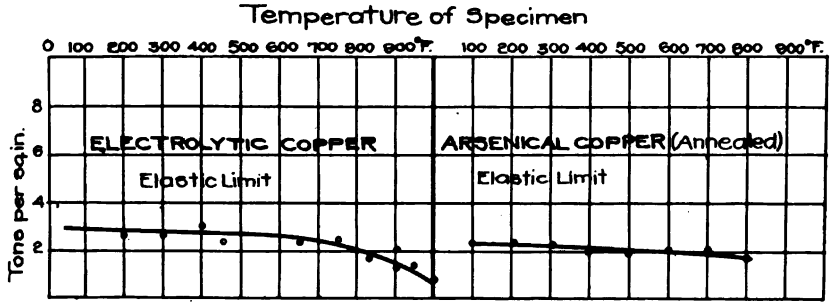


Fig. 11. Strength of Hot Copper.

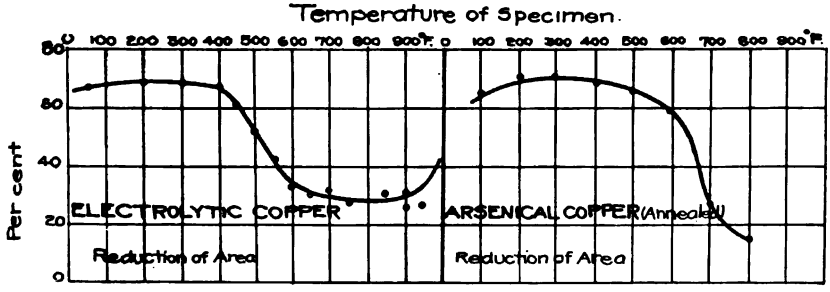


Fig. 12. Ductility of Hot Copper.

When copper is autogenously welded by the oxy-acetylene method and the specimen stretched to the breaking point, the break is found to occur at one side of the weld (Carnevah, Journ. Inst. Metals, 1912, 8, 284). This is probably due to the fact that during the preliminary heating the metal in the

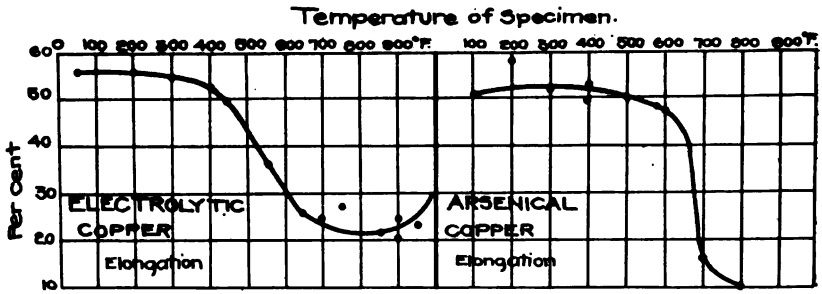


Fig. 13. Ductility of Hot Copper.

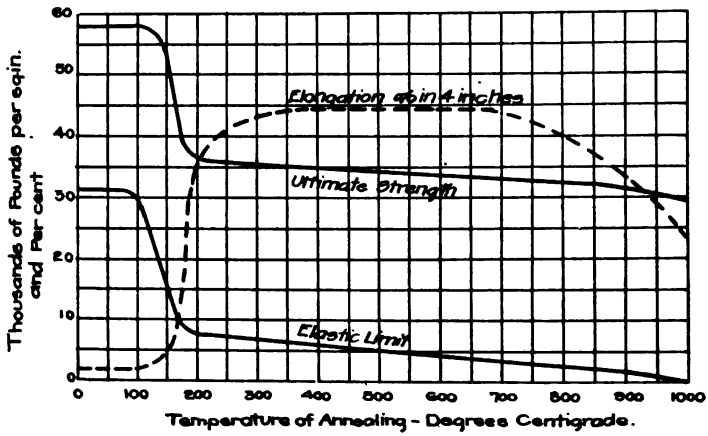


Fig. 14. Mechanical Properties of Electrolytic Copper as Affected by Temperature.

vicinity of the weld absorbs some of the gases which are abundant in the acetylene flame, and is consequently made porous and weak. The metal used for filler is usually in the form of fine wire, which is quickly melted without excessive absorption of gases. The presence of phosphorus in the copper assists in keeping down the oxidation. The high heat conductivity of copper makes the welding of large masses difficult.

The effect of annealing temperature and rate of cooling on copper is shown in Fig. 16. The conclusion to be drawn from it is that maximum ductility is obtained when the metal is heated to a bright red and quenched (Johnson, Met. & Chem. Eng., 1911, 9, 87). Copper heated above 1000° cannot be hot-worked and becomes "burnt" if it greatly exceeds this temperature. In annealing, care should be taken to exclude reducing gases which tend to deoxidize the copper and make it porous and worthless.

Fig. 15. Copper, Showing Slip Bands in a Twinned Crystal.

Cold-working increases the tensile strength and lowers the ductility. Le Chatelier states that 27 tons per square inch is the maximum tensile strength of drawn, fine copper wire. The tensile strength of the small sizes of hard-drawn wire runs relatively much higher than that of the larger sizes. (Pye, Journ. Inst. Metals, 1911, 6, 165). The increase in yield load is approximately proportional to the diameter instead of the square of the diameter as might be expected.

Cast copper subjected to shock tests shows low resilience. (Baucke, Int. Zeitschrift für Metallog., 1912, 3, 195). The resilience is greatly increased by nickel, tin, zinc, manganese and aluminum. It is desirable, therefore, where conductivity is not a factor, to add small amounts of one of the above elements to the metal. The resilience is lowered by even small amounts

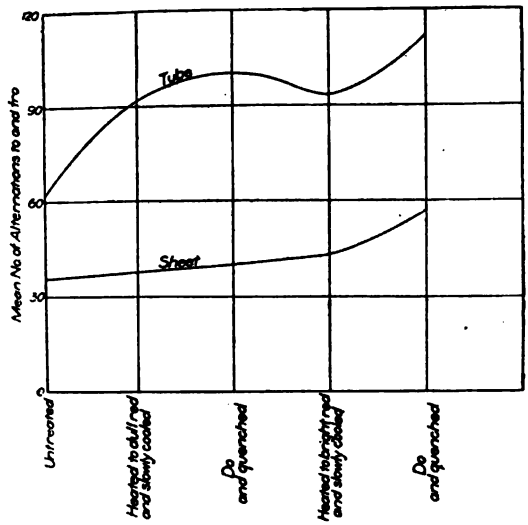


Fig. 16. Effect of Heat Treatment on Behavior Under Alternating Stresses.

of bismuth and oxygen. It will be noted later that the above elements, which improve the resilience, are soluble in solid copper, while those which are detrimental are insoluble in the solid copper. This is doubtless the explanation of the effect.

Gases in Copper.

When large charges of copper are treated in a refining furnace, conditions are ideal for the absorption of the products of combustion. The most harmful of these gases is SO_2, which, under certain conditions, may be reduced and enter the metal as sulphide. If the gases have a reducing effect, the copper may be completely deoxidized, which, as previously stated, should be avoided. Hydrogen has a hardening effect, for reasons not fully understood.

The gases absorbed by the copper are gradually expelled

as the molten metal cools, but the greatest evolution of gas occurs just as the metal solidifies, which may leave pores where gas has escaped or minute cavities which retain the gas. It is obvious that this condition is detrimental to the metal, for whatever purpose it may be intended. Guichard has heated copper in a vacuum and found that at 600 to 630° C. some CO_2, H, and N with a little CO are evolved.

IMPURITIES OF COPPER.

The one impurity which is most common in copper, as has already been stated, is oxygen which exists as minute particles of Cu_2O distributed throughout the metal, for the most part between the grains. The effect of the addition of another element depends first on its deoxidizing effect, second on the solubility of the oxide of the element in solid copper, third on the solubility of the element in solid copper without chemical combination, and fourth on the chemical affinity of the element for copper and the solubility of the chemical compound in solid copper. Too much stress cannot be put on these facts, and a knowledge of the equilibrium diagrams of copper and the various other elements is of great importance in interpreting or predicting different phenomena.

It is evident that when a metal, tin for example, remains completely dissolved in the solid copper its effect on the mechanical properties is quite different from that of a metal, lead for example, which has no solubility in solid copper and remains as metallic lead between the copper grains. This explains the general industrial use of brasses and bronzes, which come under the first class mentioned above.

It is not only necessary to consider the effect of an impurity when present alone, but also when present with other elements. The bad effect of one substance on the mechanical properties of copper may frequently be neutralized by even a small amount of a second substance; and, on the other hand, two elements, each in itself beneficial, may, when present together, prove undesirable.

Since copper alloys are not within the province of this paper, the effect of only small amounts of impurity will be considered in the following discussion.

Effect of Oxygen.

The equilibrium diagram of Cu and Cu_2O is given in Fig. 17. It is here seen that the two substances form a eutectic at 3.4 percent Cu_2O (0.36 percent O). The freezing point of this eutectic, 1064° C., was long supposed to be the true melting point of copper. The curve also shows that the oxide is insoluble in the solid metal, and thus is undesirable if present in appreciable amounts. The characteristic structure of refined copper is shown in Fig. 18. The network of oxide is seen to divide the metal into grains. Johnson (Met. and Chem. Eng., 1910, 8, 570) suggests that this is a distinct advantage when the metal is subjected to a transverse stress, for the so-called "slip bands", which occur in the metal previous to rupture,

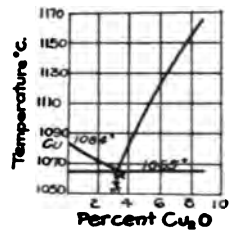


Fig. 17. Copper-Oxygen Series.

are not so easily propagated through the oxide divisions and thus make the metal more difficult to break.

Although the oxide in itself is theoretically and, if in excess, practically detrimental to copper, it performs a function which makes it desirable in small amounts. This function is two fold: First, the presence of oxygen prevents the absorption of excessive quantities of other gases; and second, when some Cu_2O is present, other impurities are in the oxidized state, in which form they have, in general, less influence in lowering the conductivity of the metal. When high conductivity is not an object, the copper may be deoxidized by tin or some other agent which improves the mechanical properties of the metal.

The determination of oxygen in refined copper by metallographic methods has been successfully done with reasonable accuracy. The most recent and quickest method is that of

Bardwell (Trans. A. I. M. E., 1913). In this case, the polished and etched specimen is placed under the microscope and the image projected upon Duplex paper to cover a circle about fifteen inches in diameter. The eutectic areas are then traced with a hard pencil, cut out and weighed. From the relative weights of the original circle and eutectic areas, the amount of oxygen can be calculated.

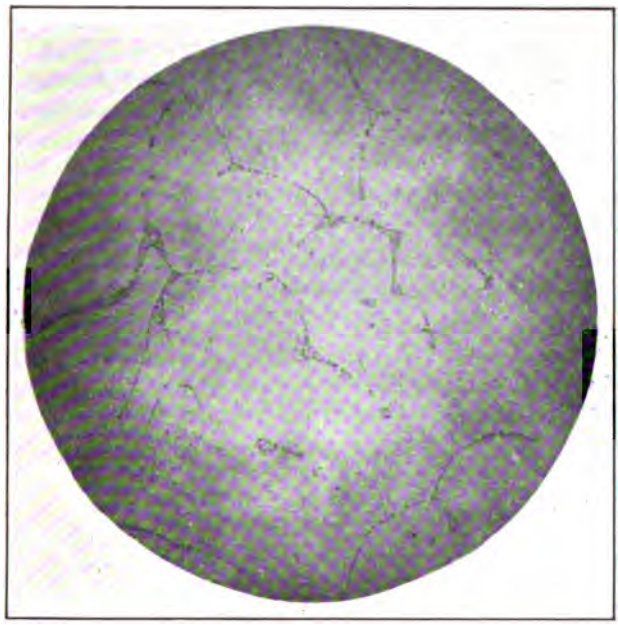


Fig. 18. Refined Copper.

Effect of Arsenic.

As seen in Fig. 19, solid copper can dissolve a maximum of four percent arsenic, probably in the form of an arsenide of copper. With larger amounts of arsenic, the solid metal will show two constituents when viewed under the microscope. As would be expected from the above facts, the presence of arsenic up to about two percent improves the mechanical properties of copper, but greatly lowers its conductivity.

Bengough and Hill (Journ. Inst. Metals, 1910, III, 34) draw

the following conclusions from tests on five bars of copper carrying arsenic varying from 0.04 to 1.94 percent.

1. Arsenic in small quantities tends to increase the maximum stress without affecting appreciably the ductility.

2. It increases their resistance to reducing gases at high temperatures.

3. Alloys with low percentages of arsenic tend to be unhomogeneous, but with increase in the arsenic this ceases to be apparent. Slight heterogeneity is probably an inherent defect in low-arsenic alloys.

4. In ordinary oxidizing atmosphere no heat treatment (for three hours or less) short of an approximation to fusion seriously affects the properties of these alloys. The only result

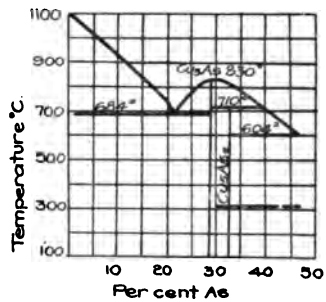


Fig. 19. Copper-Arsenic Series (Friedrich).

of annealing is to render the bars slightly more homogeneous and to lower the yield-point somewhat. This statement, however, does not apply to annealing temperatures in the neighborhood of 1000° C.

5. Alloys with less than one percent of arsenic are ruined by the action of reducing gases for three hours at 700° C. or above it; in some cases the action is apparent at 600° C.

6. The yield points of these alloys are somewhat variable and unsatisfactory.

Regarding the reducing effect of arsenic on Cu_2O authorities differ. It is probable, however, that metallic arsenic does have a slight reducing effect. The presence of arsenious oxide is distinctly harmful when the metal is heated in hot reducing gases. The tests of Bengough and Hill indicate that CO and

H penetrate to all parts of the hot metal and reduce the oxide with the formation of CO_2 and H_2O. If much oxide is present the formation and expansion of the above gases may shatter the specimen.

It has been found that the deoxidization of arsenical copper by means of ferro-silicon greatly improves its qualities. The resulting metal contains small quantities of silicon and iron which are beneficial.

The effect of arsenic in the presence of iron and silicon is well illustrated by the following table: (Johnson, Jl. Inst. Metals, 1913, X, 279).

Oxygen Percent	Arsenic Percent	Silicon Percent	Iron Percent	Tens. Str. Tons per sq. ft.	Elongation, percent on 3 inches
0.089	0	0	0	14.92	39
0.066	0.344	0	0	15.70	41
trace	0.69	0	0.43	17.05	48
0	0.35	0.80	0.24	18.25	37
0	0.38	0.36	0.13	16.20	41
0	0.39	0.22	0.13	16.30	37
0	0.35	0.15	0.07	15.85	40
0	0.36	0.20	0.06	15.60	50
0	0.34	0.02	0.035	15.55	43

In the above specimens, the ingots were found to be sound and free from porosity. The addition of the iron and silicon also increased the toughness, as shown by alternating stress tests. The deteriorating effect of hot reducing gases was found to be less marked on the specimens containing iron and silicon.

The presence of arsenic not only makes copper harder but also makes it more difficult to anneal. (Johnson, Met. and Chem. Eng., 1910, 8, 570.) Two samples of copper, one tough-pitch and the other containing 0.36 percent arsenic, were hardened by rolling and subjected to a temperature of about 200° C. for four weeks. The tensile strength of the pure copper fell off, while that of the arsenical copper was practically unaffected. Two other samples were treated at 870° C. for four hours, which caused a falling off of 44 percent in the tensile strength of the pure copper and only a 6 percent loss in the tensile strength of the arsenical copper.

Figs. 10-13 show a comparison of the mechanical properties of electrolytic and arsenical copper (0.234 percent As) at temperatures up to 900° F.

Effect of Nickel.

Alloys of copper and nickel form solid solutions at all compositions which makes nickel a desirable element for improving the mechanical properties of copper. It is particularly effective in hardening copper and raising the tensile strength. Its effect on the other properties is not so marked.

Antimony has been found to magnify the effects of nickel.

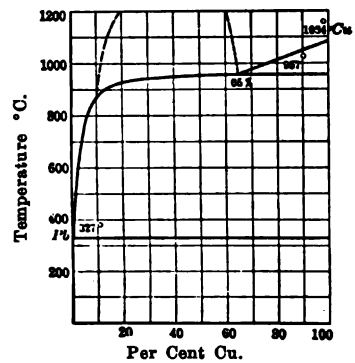


Fig. 20. Copper-Lead Alloys (Friedrich).

Effect of Lead.

The equilibrium diagram for the copper-lead series of alloys is given in Fig. 20. This indicates that lead is insoluble in solid copper. Existing as it does in the form of minute globules distributed through the copper, it has no beneficial effect, but, on the contrary, reduces the strength, ductility, and toughness of the metal. During hot-working, the lead melts and makes the metal red-short. Lead has a deoxidizing effect on copper and the lead oxide formed in the reaction is less harmful than the metal. Arsenic lessens the bad effects of lead, due to the fact that the latter dissolves in arsenide of copper.

Effect of Bismuth.

Bismuth is one of the most harmful elements in its effect on copper. Even traces of it in the metallic state make the metal brittle, either cold or hot, and prevent the drawing or rolling of the metal. When oxidized, bismuth is less harmful.

The equilibrium diagram is shown in Fig. 21.

Effect of Iron.

Solid copper can dissolve up to about three percent iron, which has a decided hardening effect. Little has been published regarding the mechanical properties of copper carrying small quantities of iron. The tensile strength and elasticity seem to be increased and the ductility greatly lowered. With iron above two percent, the alloy becomes magnetic due to the presence of free iron. Stead states (Journ. Iron & Steel Inst., 1901, II, 113) that copper with 8 percent iron has the hardness of forged steel containing 1.5 percent carbon.

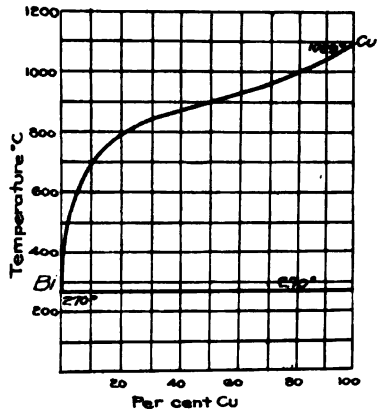


Fig. 21. Copper-Bismuth Alloys (Jeriomin).

The effect of small quantities of iron in the presence of arsenic and silicon has already been given in the table on page 16.

The equilibrium diagram is given in Fig. 22.

Effect of Antimony.

The equilibrium diagram in Fig. 23 shows that solid copper can dissolve 10 per cent of antimony in the form of antimonide of copper. In general it may be said that the effect of antimony is similar to the effect of arsenic. Small quantities (under 0.2 percent) impart certain desirable qualities, such as sounder ingots and higher tensile strength. The ductility is slightly lowered. There is reason to believe that the bad effects of both antimony and arsenic are somewhat lessened

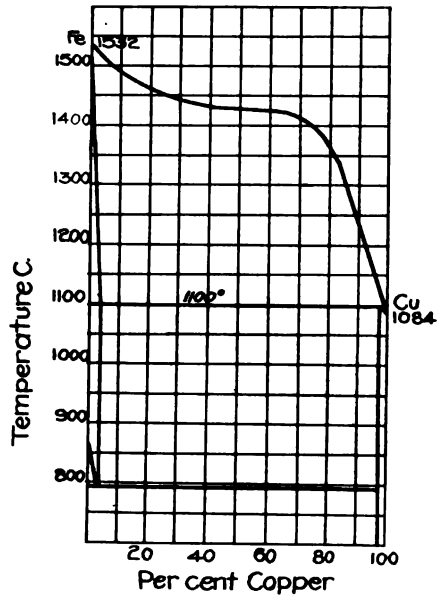


Fig. 22. Copper-Iron Alloys (Sahmen).

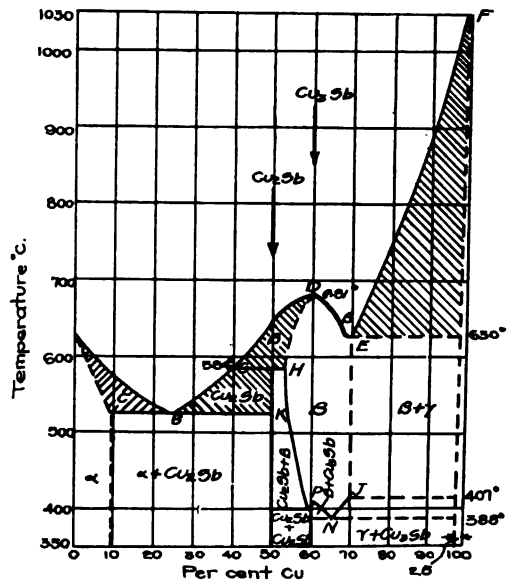


Fig. 23. Copper-Antimony Alloys (Baikoff).

when the two are present together. Antimony is beneficial during poling, as it seems to prevent the absorption of gases, rendering the ingot less likely to "spew". A large amount should be avoided, as it makes the copper hard and more difficult to roll.

The oxides of antimony are less soluble in the copper than is the antimonate of copper, and, consequently, have less effect on the conductivity.

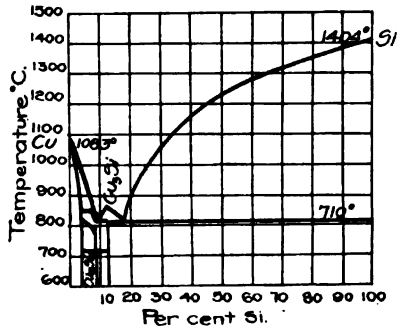


Fig. 24. Copper-Silicon Series (Rudolfi).

Effect of Silicon and Phosphorus.

The equilibrium diagrams for alloys of these two elements with copper are shown in Figs. 24 and 25. The principal use of silicon and phosphorous is to deoxidize the copper, thus making it more sound. The slight excess which remains after reducing the Cu_2O is dissolved in the copper, making it harder and increasing the tensile strength with decrease in ductility. Silicides and phosphides of copper are formed, respectively, each of which produces great brittleness when undissolved in the metal.

Effect of Manganese.

Copper forms solid solutions with manganese, which are strong and fairly ductile, but the mechanical properties of these alloys are so improved by the addition of small quantities of tin or zinc that manganese alone is seldom added to copper.

Effect of Sulphur.

Sulphur unites with copper to form Cu_2S, which, as seen by the equilibrium diagram, Fig. 26, is insoluble in the metal. It

is seen under the microscope as blue globules distributed through the copper. It can be distinguished from Cu_2O, which it greatly resembles, by etching the specimen with hydrofluoric

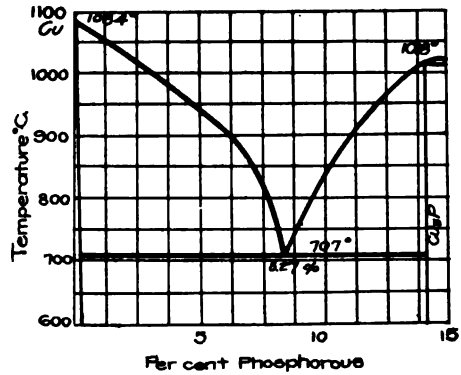


Fig. 25. Copper-Phosphorus Series (Heyn and Bauer).

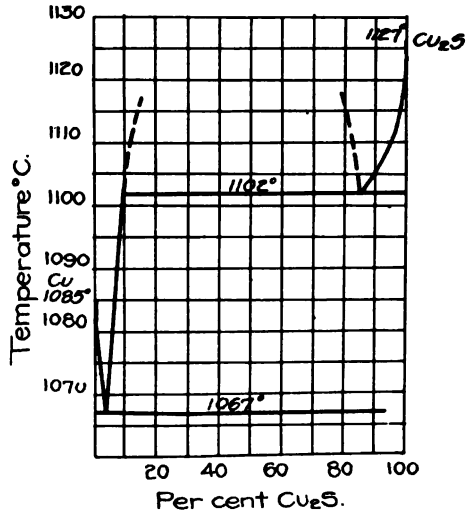


Fig. 26. Copper-Sulphur Series (Heyn and Bauer).

acid. This treatment darkens the oxide and leaves the sulphide unattacked. Copper shavings immersed in boiling sulphur are changed to sulphide in a comparatively short time, and a copper rod ¼ inch in diameter is completely changed to sulphide on boiling for three hours in sulphur.

The effect of sulphur is wholly bad, rendering the metal porous and weak.

Effects of Zinc, Tin and Aluminum.

A discussion of the effects of these elements would enter the great field of brasses and bronzes, which is not within the province of this paper. These alloys are preferred to pure copper for many purposes, because their strength is much greater than the latter and their ductility high, allowing them to be easily forged or drawn into wire.

Each forms a series of solid solutions with copper and also has a deoxidizing effect. The oxides are insoluble in the copper.

Effects of Other Impurities.

Magnesium is sometimes used as a deoxidizing agent on copper. It forms several compounds with copper, each of which, as well as the oxide of magnesium, is insoluble in the solid metal. An excess of magnesium is therefore undesirable.

Titanium is useful as a deoxidizing agent and assists in producing sound castings, but the tests of Bensell (Metall u. Erz, 1914, XI, 10, 46) indicate that an excess weakens the metal.

Tungsten and chromium are insoluble in solid copper, and although little has been published regarding the properties of these alloys, it is probable that there is at least no benefit to the copper from the presence of these metals.

Vanadium is soluble in copper, up to seven per cent. According to Norris (Journ. Franklin Inst., 1911, 171, 581) a few hundredths of a percent reduce the electro-conductivity to a marked degree and increase the elastic limit, tensile strength and ductility from ten to twenty percent.

Thallium, selenium and tellurium are each insoluble in solid copper, and even small quantities are undesirable.

Copper can dissolve ten percent of cobalt, the effect of which is somewhat similar to nickel.

CONCLUSIONS.

It is impossible to summarize all the facts brought out in the foregoing discussion, but a few general features are prominent.

It is clear that any discussion of the physical properties of copper divides itself into two general parts—viz., electrical and

mechanical properties. Unfortunately, it is true that, in general, the treatment which is most desirable from one of these standpoints is highly undesirable from the other. Pure, soft, dense metal has the highest conductivity, but its weakness is a great handicap in transmission lines. The substances which are soluble in the solid metal usually increase the strength, but always lower the conductivity. On the other hand, substances which are insoluble in the solid metal lower the conductivity to a much less degree, but usually weaken the metal. These facts should be continually borne in mind when adding a metal to copper for any purpose.

It has been pointed out that in adding any substance to copper, its effect on Cu_2O must always be considered. If the substance is used to deoxidize the copper, there next comes the consideration of the use for which the metal is intended. If high conductivity is desired, a deoxidizing agent should be chosen, an excess of which, together with the oxide formed, will be insoluble in the solid copper, and, if possible, of low specific gravity to allow it to float out of the metal after deoxidizing it. If the copper is not to be used for electrical purposes, it is usually desirable to use a deoxidizing agent, an excess of which is soluble in the solid metal.

It would seem that a period of quiescent fusion in a neutral atmosphere, possibly in an electric furnace, would allow injurious undissolved impurities to float off and produce sounder ingots.

Accurate equilibrium diagrams will greatly assist in choosing elements to produce a given effect when added to copper. The great lack in existing diagrams is the absence of solubility curves for the solid state. Such curves are a guide not only in selecting a proper amount of an alloying element, but also in determining a proper annealing temperature.

The important subject of heat treatment of alloy copper has hardly been touched on in this paper, because little information is obtainable. It is undoubtedly true that proper heat and mechanical treatment may make an otherwise worthless alloy valuable, and, on the other hand, improper treatment may ruin a good alloy.

The leading effects of various elements, when added to

copper, have been discussed, but little reference has been made to the combined effects of two or more elements. Here again there is little definite information to be had. The field is almost unlimited, and it is probable that systematic research based upon the equilibrium diagrams for the binary alloys would open the way for improvements in the mechanical properties of copper.

DISCUSSION

Mr. Addicks.

Mr. Lawrence Addicks,* Mem. Am. Inst,. M. E., stated that he wished to call attention to the influence of the method of casting upon the effect of oxides. He said that, in present copper refinery practice, all the castings are made in shallow molds, which permits a considerable surface of the copper to be exposed to the air. He stated that he thought the time was coming when a little more money would be spent upon casting for the sake of producing copper free from oxides. This he said could be accomplished by casting the bars on end, so that the area exposed to the air would be small, and then the part containing the absorbed oxygen could be cut off and remelted.

Mr. Ricketts.

Mr. L. D. Ricketts,† Mem. Am. Inst. M. E., asked if there was any other way of reducing cuprous oxide in refined copper than by poling.

Mr. Addicks.

Mr. Addicks replied that he thought there would be no difficulty in using gas for this purpose and that it might in time be used, since the price of wood was going up in the East, whereas the price of coal had not been very much affected.

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† New York, N. Y.

Paper No. 181

BORONIZED CAST COPPER.

By

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"Boroflux" as a deoxidizer of cast copper is now used in a large number of foundries, both in the United States and abroad. Based on sound theory and easily carried out in practice, the "boronizing" of copper is bound to become the standard method wherever cast copper of good mechanical properties and high electrical conductivity is desired.

The theory on which the method is based is as follows:

Copper in melting absorbs gases which, on cooling, are set free, causing porosity. These harmful gases are oxygen, sulphur dioxide and carbon dioxide, singly or in combination. An ideal deoxidizer for copper should eliminate these gases and, at the same time, have no affinity for copper. The latter condition is of importance, as it allows the addition of an excess of the deoxidizer without fear of contamination of the copper. Boroflux satisfies these conditions and is the only flux which satisfies them both.

Boroflux can be most generally defined as a material which contains boron in a state of oxidation below that of boric anhydride. Such a material takes up free oxygen and reduces oxygen-containing compounds; in this reaction it is transformed into boric anhydride, which, being fluid at the temperature of melted copper, comes up to the top of the metal as such, or carrying in solution different metallic oxides, especially cuprous oxide.

Different compounds of boron would come under this general definition of boroflux, but up to the present, only two have been used commercially, namely, boron suboxide and boron carbide. From the point of view of ease of manipulation and cost, the boron suboxide flux is preferable, but recently, due to a

temporary difficulty in obtaining raw materials from Europe, the carbide was used to some extent.

Boroflux can be added to the metal in different ways, depending on the nature of the furnace and on the individual preference of the melter. The flux can be placed on the bottom of the pot, mixed with charcoal and stirred into the copper after the metal is melted; or else the flux is placed in the ladle, copper from the melting pot poured on the top of the flux, and the whole thoroughly stirred. It is important, however, to observe the following principles: The metal must be superheated to about 1250°, so as to allow the reaction between the flux and the gases to proceed rapidly; the copper must be covered with a layer of charcoal, so as to prevent as much as possible the absorption of gases; and wherever high electrical conductivity is essential, great care must be taken that the metal melted should be pure copper and that no metallic impurities be introduced during the melting or stirring.

Three quarters of one percent are usually added. An average conductivity of over 90% is regularly obtained.

The efficiency of the deoxidation of copper by means of Boroflux is well illustrated by a recent investigation by F. O. Clements, presented before the American Institute of Metals at the meeting of 1914. In this investigation copper was remelted a number of times until it was thoroughly burned and then deoxidized by boron suboxide. The following table is a part of one given in Clements' article:

	Virgin Metal	First Heat	Fourth Heat	Boron Suboxide
A. B.	1515	850	334	2007
R.	100%	97%	96%	103%

A. B. Average number of alternate bends.

R. Resistance offered by test bar to the bend, given in percentage, assuming the virgin metal to be 100%.

As the table shows, the mechanical properties of the burned metal after being deoxidized by Boroflux are superior to those of the virgin metal.

Of great interest is the attached X-ray photograph taken by Dr. W. P. Davey, of the General Electric Company, with a Coolidge tube. The photograph attached was taken through ¾

inch cast block copper, one piece cast without flux, the other with the help of Boroflux. The photograph shows the porosity

X-ray Photograph showing Porosity of Ordinary Cast Copper and Solidity of Copper Cast with Aid of Boroflux.

of ordinary cast copper and the solidity of copper cast with the aid of Boroflux, and visualizes the action of the flux in the best imaginable way.

The action of Boroflux raises a number of questions which are not answered by the simple theory given above. Here, as is often the case, practice is ahead of theory. A complete description of the reaction between Boroflux and copper would require the understanding of delicate equilibria and, in fact, would involve the whole problem of the influence of oxygen on copper.

It is generally assumed that oxygen hardens copper, and I had occasion to observe that copper completely free from oxygen is very soft indeed. The copper deoxidized by Boroflux is, however, hard enough so that no trouble is experienced in machining it. In other words, the probability is that Boroflux does not eliminate oxygen completely but that a fortunate equilibrium is established in which a sufficient amount of oxygen is left to cause a desirable degree of hardness.

As Boroflux has no affinity for lead, tin, zinc, the important metals used in the brass foundry, it is also an excellent deoxidizer for all the copper alloys containing the above elements. Boroflux is being used for this purpose and gives results superior to other deoxidizers. However, while in copper casting Boroflux is without rival, in copper alloys the superior results obtained must in each case be weighed against the somewhat higher cost.

There is hardly any doubt that there is a field for the application of Boroflux in the metallurgy of copper, but outside of a few weak attempts nothing worth recording has been done as yet.

For the history of the discovery of this method and its progress since inception, the reader may be referred to articles the writer has published: "Cast Copper of High Electrical Conductivity", Transactions of the American Electrochemical Society, Vol. XVIII, 1910; and "Progress of Work on Boronized Copper", Transactions of the American Institute of Metals of 1912.

DISCUSSION

Dr. H. O. Hofman,* Mem. Am. Inst. M. E. (by letter), said that the idea of the author of using boron or an oxide of a lower state of oxidation than boric anhyride in making dense copper castings is one which practical experience has pronounced a success. Investigations Dr. Hofman.

* Mass. Inst. of Technology, Boston, Mass.

Dr. Hofman.

into the mechanical properties and the electric conductivity of copper cast with boroflux bear out this statement. The chemical effect of the reagent, however, has not been made as clear as is desirable. The author states that boroflux eliminates from copper oxygen, sulphur dioxide, and carbon dioxide.

The work of Clements quoted shows that boroflux reduces cuprous oxide provided that in the experimental fusions the necessary care was taken to exclude all contamination with sulphur.

The solubility of sulphur dioxide in copper increases, on the whole, with the temperature and the purity of the metal. Does the use of boroflux decrease the dissolving power of copper for sulphur dioxide? This is a question that can be answered only by special research. If the answer is negative, there remains another explanation for the good effect of the flux. Molten copper can hold in solution both cuprous sulphide and cuprous oxide, which react upon one another when the temperature is lowered, and give copper and sulphur dioxide. If boroflux oxidizes cuprous sulphide and reduces cuprous oxide to the limits in which they will not react upon one another when the copper cools and finally solidifies, no sulphur dioxide will be set free to render the casting porous.

As regards carbon dioxide, it is generally held that this gas is insoluble in molten and in solid copper. It will require very strong experimental and practical evidence to put aside the researches of Hampe, Stahl, and others, and the experience of many refiners. I may add that the absorption of gases by copper has been recently discussed by Dr. W. Stahl in Metal und Erz, 1915, XII, 181-184 (Abstract Engineering and Mining Journal, 1915, C, 52) who is probably the best living authority upon this subject.

Paper No. 182

THE METALLOGRAPHY OF COPPER.

By

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In dealing with the structure of copper, the presence of more or less oxide of copper is so important that it is necessary, first of all, to show the effect of copper oxide on copper.

The thermal diagram, Fig. 1, was published by Heyn[1] in 1900. The freezing points of mixtures up to 9 per cent Cu_2O were determined as shown. Thus the freezing point of copper, 1084° C., is depressed by the addition of Cu_2O, progressing until we reach a minimum at 1065° C. and 3.5% Cu_2O. A further increase in Cu_2O raises the freezing point of the mixture. Thus *A B* shows the lowering of freezing of copper from 1084 to 1065° C. as the alloy is enriched in Cu_2O, while *C B* shows that the temperature at which the excess Cu_2O freezes out is lowered as the alloy is impoverished in Cu_2O. The intersection of these two curves is the eutectic, or the alloy with the lowest freezing point.

R. E. Slade and F. D. Farrow, in an investigation of dissociation pressures and melting points of the system copper-cuprous oxide,[2] published the diagram, Fig. 2. This shows that mixtures above 20 per cent Cu_2O separate out into two conjugate liquids whose compositions are given by the solubility curves *C G* and *F H*.

Thus, at 1400° C. the upper layer contains 92 per cent Cu_2O and the lower one 23 per cent Cu_2O. At 1195° C., where the solubility curve cuts the freezing point curve, the upper

[1] Mitteilungen aus den Königlichen Versuchsanstalten zu Berlin, XVIII, 315 (1900). Metallographist, VI, 49 (1903). Zeits. für anorgan, Chemie, 39, p. 11 (1904). Metallographie von Heyn u. Bauer, II, p. 31.

[2] Proc. Royal Society of London, 87, Series A, p. 524. (1912)

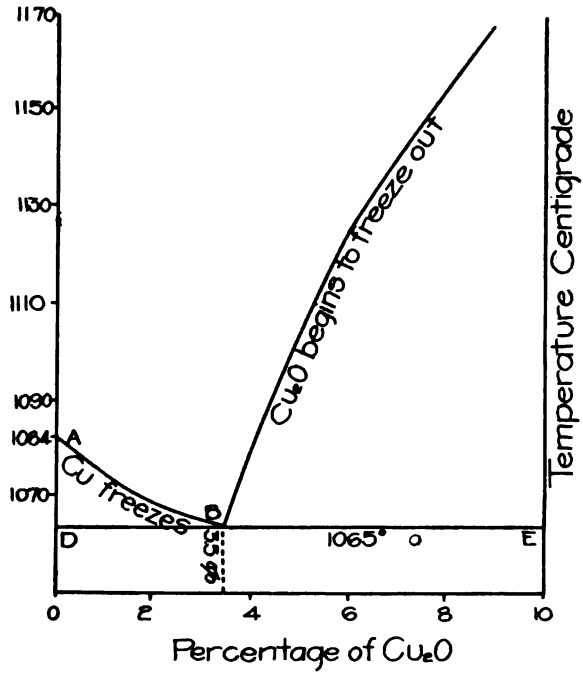

1170
1150
1130
1110
1090
1084
1070
A
Cu freezes
B
Cu2O begins to freeze out
Temperature Centigrade
D
3.5%
1065°
E
0
2
4
6
8
10
Percentage of Cu2O

Fig. 1.

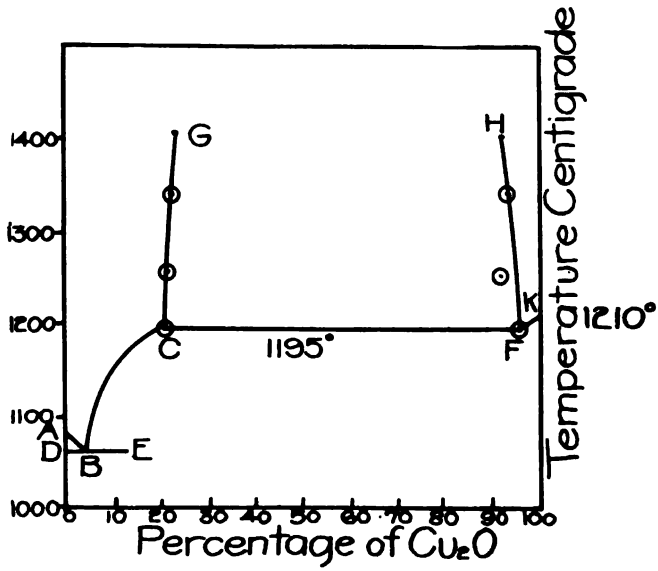

1400
1300
1200
1100
1000
G
H
K
C
1195°
F
1210°
A
D
B
E
Temperature Centigrade
0
10
20
30
40
50
60
70
80
90
100
Percentage of Cu2O

Fig. 2.

layer contains 95.5 per cent Cu_2O and the lower one 20 per cent Cu_2O. The freezing point of Cu_2O is 1210° C. The microstructure of the system Cu-Cu_2O was shown by Heyn, whose photographs and curve are reproduced in an article by Hofman, Green and Yerxa,[3] entitled "A Laboratory Study of the Stages in the Refining of Copper". Herein are found photographs of fractures of copper at different stages in refining, together with micrographs and the suggestion that poling could be controlled by the microscope, the eutectic being determined by planimetric measurements and the oxygen determined thereby.

Fig. 3. Alloy Containing About 1.7 Percent Cu_2O. (Magnified 60 diameters.)

Fig. 3 x 60 diameters shows an alloy containing about 1.7 per cent Cu_2O. The light dendrites and grains are the copper which began to freeze out when the alloy cooled to the temperature of the curve *A B*. The dark ground-mass is the eutectic, a mechanical mixture of Cu and Cu_2O, which freezes at the constant temperature *DBE*, 1065° C.

Fig. 4 x 60 diameters shows an alloy containing more than

[3] Trans. Amer. Inst. Mining Engineers, Vol. 34, p. 671. (1904)

Fig. 4. Alloy Containing Over 3.5% Cu_2O. (x 60 diam.)

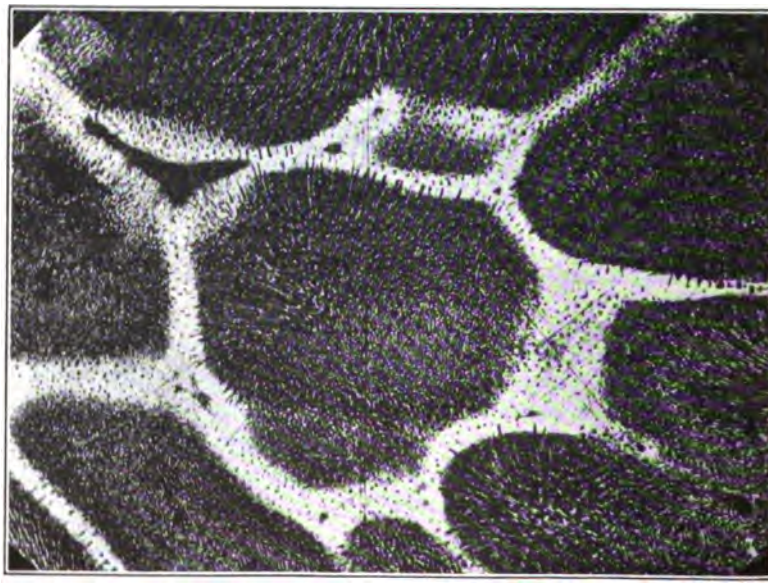


Fig. 5. Eutectic Alloy, 3.5% Cu_2O. (x 90 diam.)

3.5 per cent Cu_2O. The black dendrites are the excess Cu_2O, which began to freeze out when the alloy reached the temperature of the curve *C B*. The ground-mass, as before, is the eutectic, containing 3.5 per cent Cu_2O, freezing at 1065° C.

Fig. 5 x 90 diameters shows the structure of the eutectic alloy, 3.5 per cent Cu_2O, etched with nitric acid and slightly repolished. It has a distinctly granular structure, each grain being shot with filaments of the oxide, which become distinctly coarser towards the boundaries of the grains.

E. S. Bardwell, in a paper on the metallography of refined copper,[4] gives a method of developing the structure by heating the polished specimen in hydrogen to about 300° C. The image is projected directly as a piece of "duplex" paper so as to cover a circle of 15 to 16 inches in diameter. The outlines are traced lightly with a hard pencil. The copper areas are next cut out with a sharp knife, leaving a network representing the eutectic. The two lots of paper are then weighed and the oxygen content computed.

F. Johnson, in discussing the effect of silver, bismuth and aluminum upon the mechanical properties of tough-pitch copper containing arsenic,[5] shows in his metallographic study how the globules of Cu_2O are prone to isolation in arsenical copper. In another paper on the influence of impurities in tough-pitch copper,[6] he points out that antimony occurs in two forms in tough-pitch copper: (1) in solid solution in the copper; (2) partly as an insoluble compound with oxygen, in the form of slate-colored oxidules, distinguished from Cu_2O, which appears as light-blue oxidules. The latter with the antimonial oxidules form a ternary eutectic with the solid solution. He also shows that antimony up to 0.5 per cent has no influence on the hot-working; and that tough-pitch arsenical copper (0.4% As) is slightly hardened for hot-rolling by 0.2 percent Sb, but its mechanical properties are unimpaired.

In general, the structure of arsenical copper is similar to that already described. Fig. 6 x 285 shows dendrites of copper oxide in excess of the eutectic. Fig. 7 x 285 shows the structure

[4] Trans. Amer. Institute of Mining Engineers, Vol. 46, p. 742. (1913)
[5] Journal Institute of Metals, Vol. IV, p. 163. (1910)
[6] Journal Institute of Metals, VIII, p. 192. (1912)

Fig. 6. (x 285 diam.)

Fig. 7. (x 285 diam.)

of tough-pitch, while Fig. 8 x 285 is that of over-poled copper, all containing about 0.5 per cent As, and cast in the form of small ingots about one inch square. The over-poled copper is distinctly porous, being full of tiny blow-holes and often showing distinct spaces between the grain boundaries.

In a paper describing a method of improving the quality of arsenical copper,[7] Johnson states that silicon can be added in considerable excess of the quantity required to effect deoxida-

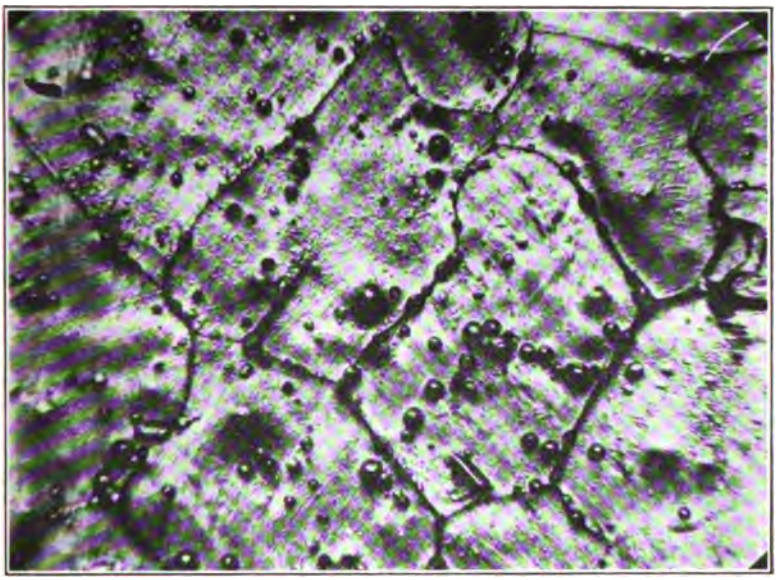


Fig. 8. (x 285 diam.)

tion, without producing hot-shortness. In pure copper, silicon does not seriously lower the electrical conductivity. Johnson heated specimens in hydrogen at 780° C. and showed that it is the oxygen that renders copper susceptible to the disintegrating influence of reducing gases at high temperatures. Now, as arsenic has an isolating effect on the Cu_2O particles, non-arsenical copper is more prone to rottenness due to reducing gases. For locomotive staybolts, copper is toughened and given a better resistance to reducing gases by the addition of silicon.

[7] Journal Institute of Metals, Vol. X, p. 275. (1913)

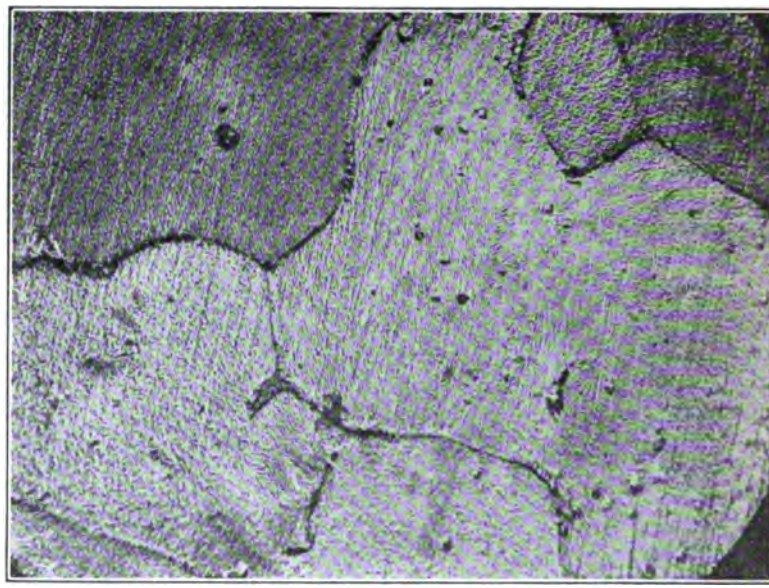


Fig. 9. Pure Deoxidized Copper as Cast. (x 230 diam.)

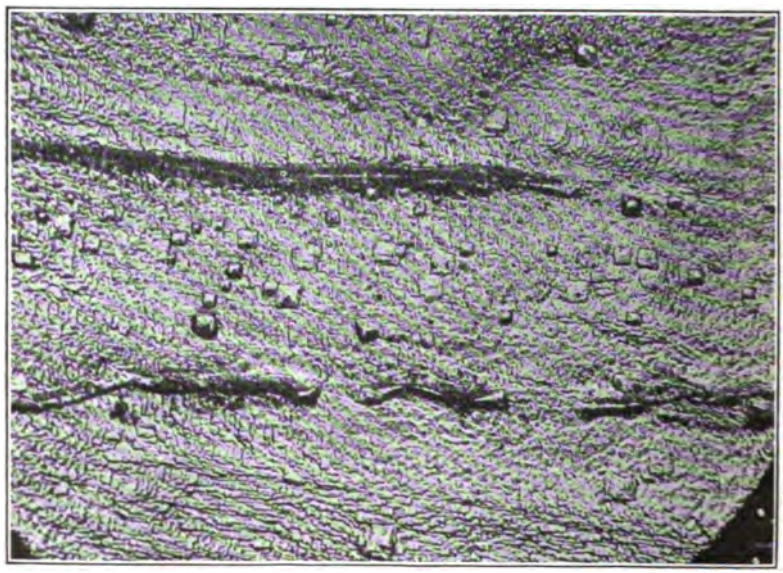


Fig. 10. Etch-Pits. (x 425 diam.)

THE STRUCTURE OF COPPER AND THE EFFECT OF COLD WORK.

Pure deoxidized copper consists of irregular crystals or grains as shown in Fig. 9 x 230. There is a trace of Cu_2O, as small globules, between the grains. The internal structure of the grains is revealed by deep etching. Fig. 10 x 425 shows the same copper deeply etched. The black streaks are the grain boundaries, containing some Cu_2O. The copper itself shows cubic etch-pits. When such metal is strained beyond the elastic limit, the grains are elongated and drawn out by means of slip-lines

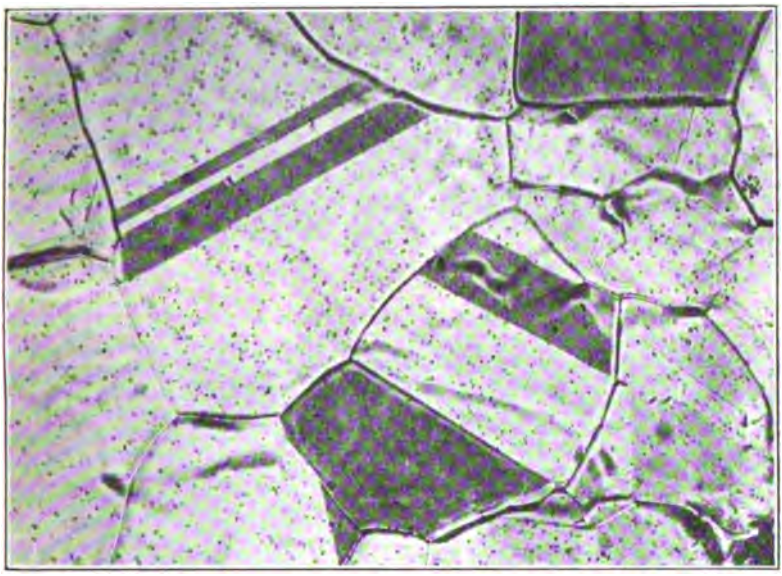


Fig. 11. Cu Annealed in Hydrogen (x 500 diam.)

and slip-bands, within each grain, which are oriented similarly to the etch-pits. The greater the work, the more are the grains drawn out.

On annealing, the grains tend to rearrange themselves and show marked twinning. Fig. 12 x 500 diameters shows the structure of a rod one-half inch in diameter, after annealing. The multiple twinning is distinct, but the grain boundaries are not distinct by this method of etching with nitric acid. Using a modification of Bardwell's method of etching in hydrogen and

annealing at the same time, both grain structure and twinning are revealed. Thus, Fig. 11 x 500 shows a piece of cold-drawn copper tubing heated to 1000° C. in hydrogen.

Baucke,[8] in a paper on some recent micrographical investigations on copper, deals with the influence of annealing on the grain size of cold-drawn material. The grain size was measured after annealing for varying periods of time at temperatures from 100° to 1050° C. He found the minimum size of grain at 350° C., followed by a slow increase up to 700° C. Between 700 and 800° C., the grain size doubles, while above 900° C. the increase is more rapid still. In regard to the oxide in copper, cold work destroys the eutectic structure and the oxide is strung out. Reheating of cast copper produces no change up to 700° C. At 800° C. the Cu_2O tends, in time, to ball up, while at 900° C. this balling up into globules is very rapid.

Figs. 18 and 19 are taken from a paper by Captain C. Grard on the industrial application of microscopic metallography for controlling the work put on copper and brasses.[9] In Fig. 18 the amount of cold work in the specimen is derived from $\left(\frac{S-s}{s} \times 100\right)$; where S is the original cross-section, and s the new cross-section. The elongation falls rapidly from 43 per cent to 5 per cent with 20 per cent of cold work. Beyond this there is but little change. The elastic limit increases rapidly up to 60 per cent of cold work, beyond which point there is little increase. The tensile strength curve is similar, there being only a slight increase beyond 100 per cent of cold work.

In Fig. 19, annealing begins to show marked effect on the physical properties above 100° C. and is practically complete at a little above 200° C.

The effect of cold work can be seen in the following photographs.

Fig. 12 x 500 shows the structure of an annealed rod one-half inch in diameter, longitudinal section. The grain varies somewhat, but the twinning is marked. Fig. 13 shows the same rod drawn to 0.4 inch in diameter. The grains are distinctly

[8] Proc. Internat. Assoc. Testing Materials, Vol. II, Sec. 11, No. 14. (1912)

[9] Proc. Internat. Assoc. Testing Materials, Vol. II, Section 11, No. 15. (1912)

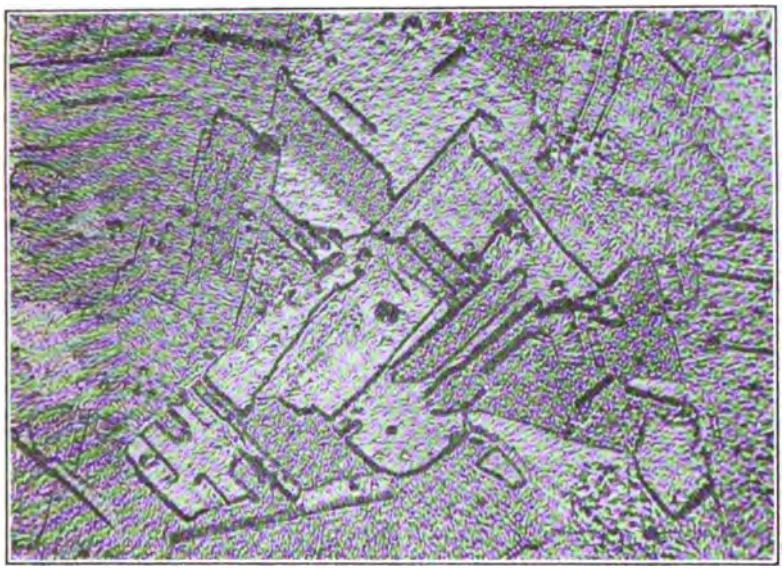


Fig. 12. Half-inch Rod Annealed (x 500 diam.)

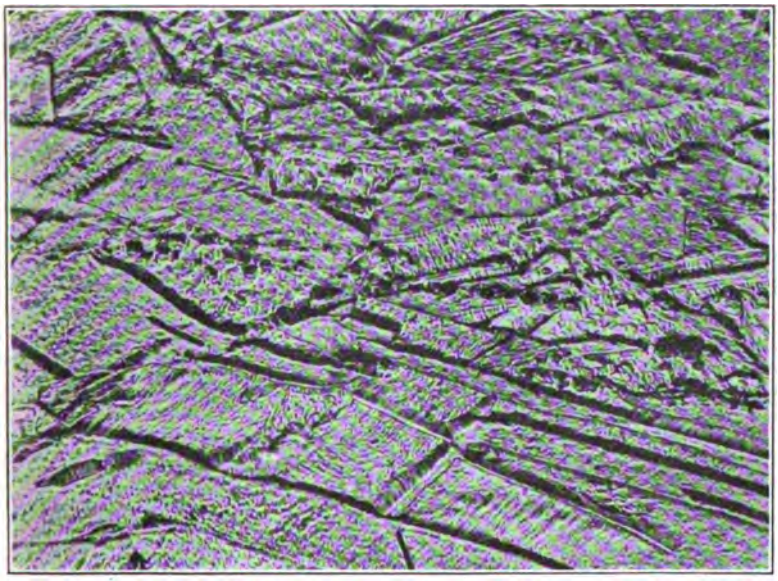


Fig. 13. Half-inch Rod Drawn to 0.4 in. Diameter (x 500 diam.)

elongated, many of them showing a cross-hatched effect, due to the slip-lines. The black globules are copper oxide, originally round the grain as part of the eutectic, but, due to work and annealing, now strung out into lines.

Fig. 14 shows the rod drawn down to 0.3 inch in diameter, giving a further elongation of grain and more slip lines. It is practically impossible to see the difference between grain boundaries and twin planes, in most cases.

Fig. 15, drawn to 0.2 inch in diameter, shows a further elongation of grain; while in Figs. 16 and 17, drawn to 0.1 inch and 0.05 inch respectively, the structure looks fibrous, due to the extreme elongation of the grains.

From the above it can be seen that the greater the reduction, the more the grains are drawn out. The reason for the increase in strength and decrease in ductility has long been a matter of dispute. Recently, the "Amorphous Theory" of Beilby has gained much support, and confirmation. This has been ably reviewed by Rosenbain in a paper[10] entitled "Metals, Crystalline and Amorphous". In short, the amorphous theory holds (a) that polishing produces a film of amorphous metal as the surface; (b) when a metal is strained, the slip-lines and slip-bands produced are covered with a film of amorphous metal, which is less dense and much harder than the crystalline variety —this explains changes in hardness, density, etc., of strained metal; (c) where the constituent crystals of a metal meet, thin films of residual liquid metal will remain under circumstances which render them incapable of crystallizing, so that they will constitute thin films of under-cooled liquid or amorphous metal, rolling of the ingot into $\frac{5}{8}$-inch round rods.

THE EFFECT OF HOT WORK.

The effect of hot work upon the structure of copper was studied by examining specimens of the metal taken during the rolling of the ingot into $\frac{5}{8}$-inch round rods.

The first thing noted was that the Cu_2O of the eutectic was drawn out into long strings of rounded globules. On examining the structure of the metal after different degrees of reduction, it was found that all structures resembled those of annealed metal.

[10] Engineering, Vol. 96, pp. 509-537. (1913)

Fig. 14. Drawn to 0.3 in. Diameter (x 500 diam.)

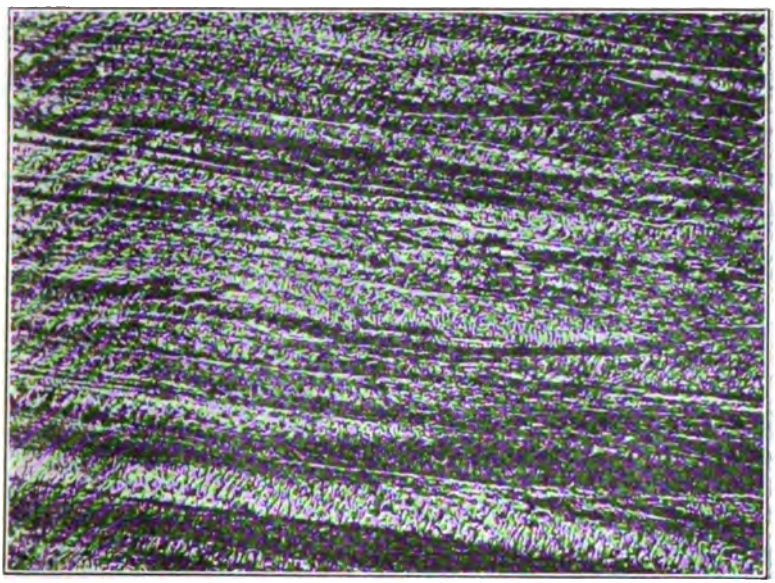


Fig. 15. Drawn to 0.2 in. Diameter (x 500 diam.)

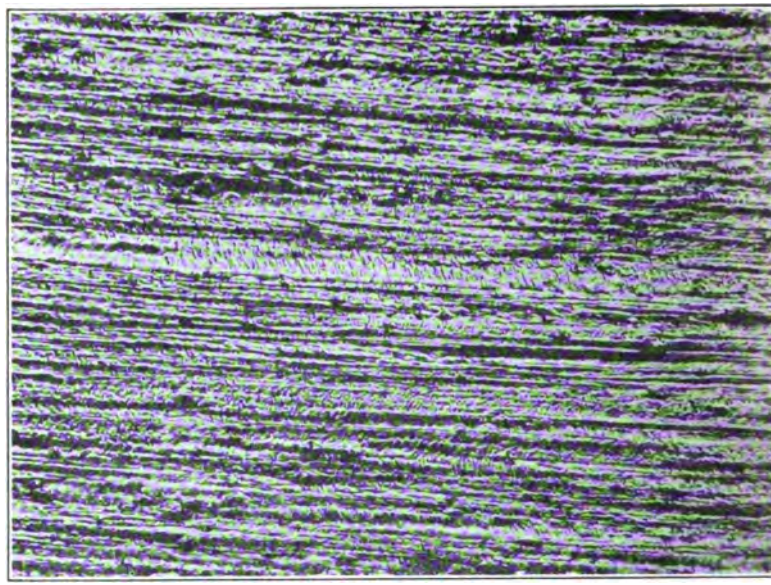


Fig. 16. Drawn to 0.1 in. Diameter (x 500 diam.)

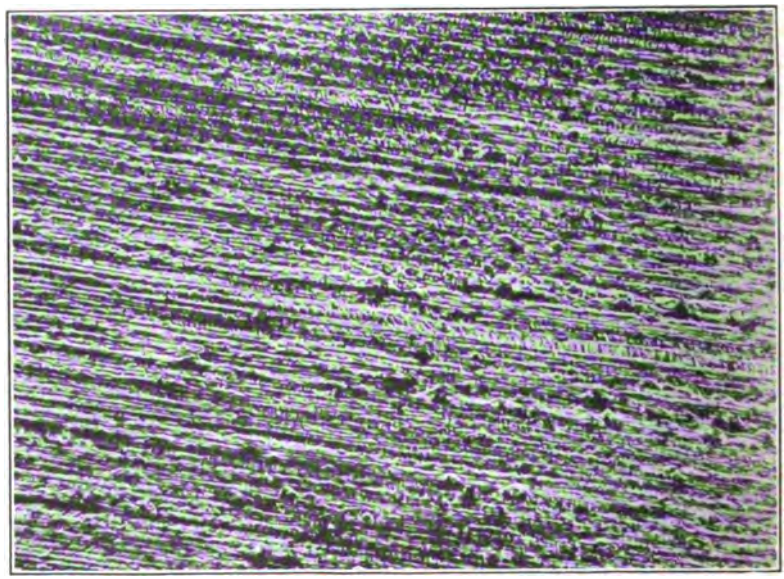
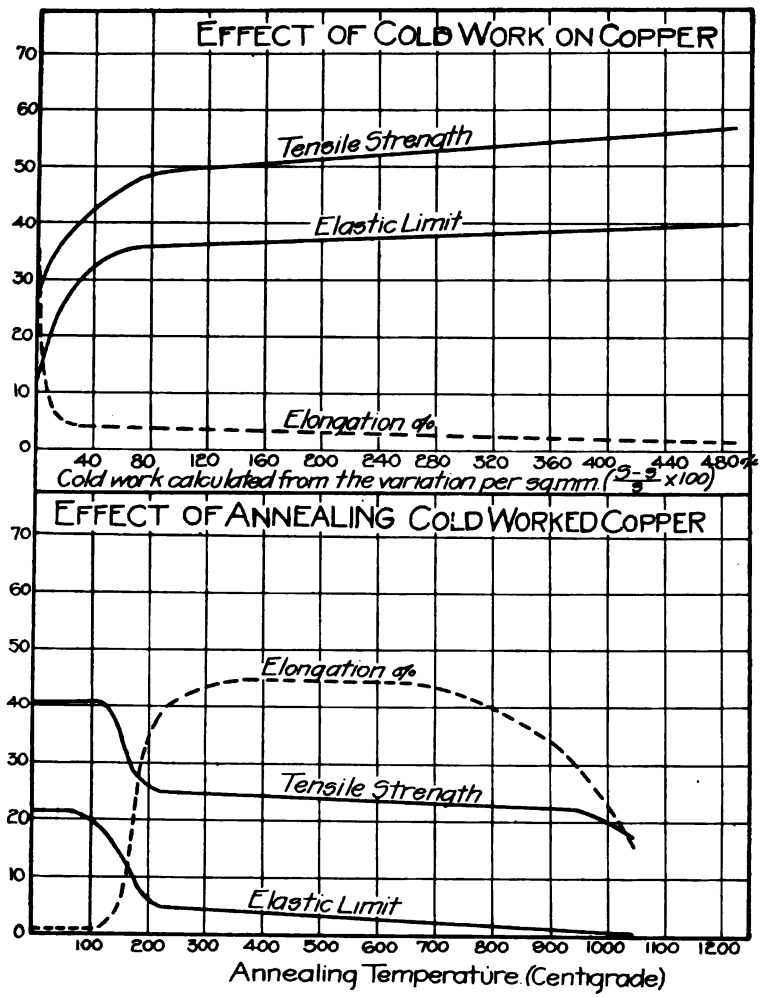


Fig. 17. Drawn to 0.05 in. Diameter (x 500 diam.)

While the grains became progressively smaller they showed no elongation, because, after each pass through the rolls, the heat



Figs. 18 and 19.

of the metal was enough to cause a rearrangement of the grain, in other words, to give complete annealing.

The structure of electrolytic copper has been examined by

Faust[11] who finds that the crystallites arrange themselves parallel to the lines of the current. The layer at first deposited consists of very numerous small crystals, but only a few continue to grow. He says that electrolytic copper, like worked copper, develops twinning planes when annealed, indicating the presence of an internal stress, the existence of which is rendered probable by the known properties of thin electrolytically deposited films. However, the presence of twinning in fresh electrolytic copper has been shown by Campbell in a paper on the structure of metals,[12] while native copper shows the same thing. When wire-bar ingots are examined, twinning is not infrequently met with.

In conclusion, reference must be made to a paper by F. Johnson[13] on wrought copper. He first discusses the structures of under-poled, tough-pitch and over-poled copper; then the effect of mechanical work. In regard to the properties of copper at high temperatures, he reviews the work of Roberts-Austen in the second report of the Alloys Research Committee of the Institution of Mechanical Engineers, and of F. W. Webb on locomotive fire-box stays,[14] and of the Royal Technical Research Commission of Berlin, 1898. In short, the strength falls as the temperature rises, the effect being very marked at 200 to 300° C. Bengough and Hudson[15] in a paper on "The Tensile Properties of Copper at High Temperatures", Huntington[16] on the effects of temperatures higher than atmospheric on tensile tests of copper and its alloys, and Hughes[17] on non-ferrous metals in railway work, deal with the physical properties of copper when hot. Guillet and Bernard[18], from shock tests, find a maximum resilience near 100° C. and a maximum brittleness at 300 to 400° C.

[11] Zeits. für anorg. Chemie, LXXVIII, p. 201. (1912)
[12] Metallurgie, Vol. IV, part 23. Fig. 891.
[13] Metallurgical & Chemical Engineering, Vol. IX, p. 396. (1911)
[14] Proc. Institution of Civil Engineers, London, Vol. CL, part IV. (1902)
[15] Journal Institute of Metals, XII, 56.
[16] Journal Institute of Metals, VIII, 126; XII, 234.
[17] Journal Institute of Metals, VI, 74.
[18] Comptes Rendus, CLVI, 1899.

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DISCUSSION

Prof. G. H. Clevenger,* Mem. Am. Inst. M. E., stated that all copper metallurgists were indebted to Professor Campbell, Mr. Bardwell, and others who had been working in this purely scientific field of metallurgical endeavor. He also called attention to the fact that formerly refining of copper, referring to the furnace operation of melting the cathodes, was more or less an art, since rough qualitative tests, such as the behavior of a test bar as regards bending and breaking, were depended upon to determine when the copper had reached the right pitch. Now, through the science of metallography copper refining or melting has ceased to be an art and is a very definitely defined science. Consequently, the operator, when anything goes wrong, can ascertain exactly what the difficulty is.

* Stanford University, Calif.

Paper No. 183

METALLURGY OF COPPER IN JAPAN.

By

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INTRODUCTION.

Japan, one of the oldest nations in the world, has not been unfamiliar with mining and metallurgy. This science was known and practiced from of old, but being limited to the domestic needs, its development was in consequence comparatively slow. In the days of the Tokugawa Shogunate, foreign trade having been prohibited, the export of mining products was completely stopped. The gold, silver, copper, iron, and other mines in those days were all worked by the Government, and even after the Restoration, when foreign trade was opened, the principal mines in the country continued to be worked by the Government, but in such an uneconomical way that none of them proved to be remunerative. Such mines as were worked by private capital also failed to prosper, on account of the lack of sufficient funds and the primitive methods employed.

As early as the year 708, copper coins were minted in Japan and our people have been acquainted, for the last four hundred years, with a smelting process called "Mabuki".

In writing on the metallurgy of copper in Japan, as contributing to the symposium, I first feel it is necessary to state that I will confine myself principally to the advance as made during the past decade in the Furukawa Company.

THE MABUKI PROCESS.

The Mabuki process presents an interesting analogy to the Bessemer process. It has been gradually improved from generation to generation to its present state. It is the primitive

process useful in operations of small proportions, and is quite simple and economical for such mines as may be producing about 200 tons of copper a month.*

The cost of treatment by the Mabuki process is given as not being higher than ½ cent (U. S. currency) per lb. of copper.

In the construction of the Mabuki hearth, an excavation of 10 ft. in diameter by 6 ft. in depth is made in the ground, which is lined with brick, stone or slag brick to a thickness of about 1½ ft., care being taken to have a passage in the bottom permitting the escape of any steam arising from the moisture in the lining. The surface of the lining is coated with clay about 6 in. thick. The cavity is then filled brasque and well tamped, leaving a cylindrical space of a diameter of 3 ft. and a depth of 1½ ft. at the centre of the cavity. This cylindrical space is the Mabuki-hearth.

The hearth should be thoroughly dried with wood, charcoal or molten slag to prevent an explosion which might otherwise occur during the blowing operation. The hearth is covered with a hemispherical dome made of clay 1½ ft. high, provided with a tuyère hole and a working door. In front of the working door, there is a small slag reservoir lined with clay.

The tuyère, a sheet-iron pipe of about 2½ in. diameter, is coated with clay at the end to protect it from the splashed particles of molten matte. The molten matte is poured into the hearth, charcoal is placed on top, and then the air blast is turned on. Sometimes heavy oil is injected by the blast. As soon as oxidation begins, slag is gradually formed, and is raked out from time to time. More matte is added to keep a nearly constant level of molten mass in the hearth. In this manner the operations are repeated until 3 to 4½ tons of the matte are charged. The slag-forming period takes about 13 to 14 hours. At the end of the period, all of the slag is skimmed in order to give the blast full play on the exposed molten matte. The oxidation continues about 4 hours. When this period is over, charcoal is added (or heavy oil is injected) to maintain the proper temperature for the reaction process, which is final for the Mabuki process and takes about 5 hours. The blister copper

* Reference to a ton throughout this paper means one of 2000 lbs.

thus obtained averages about 98.5%. On account of the formation of iron oxides during the operation, the silicious lining is so extremely corroded as to require frequent repairs. After the copper is tapped out, the hearth is repaired and dried for the next series of operations. The repairing requires about 2 hours. The blast pressure is 9 to 12 oz., and about 1.6 tons of blister copper are produced from about 4.5 tons of 40% matte. Nearly 24 hours are required to finish a whole cycle of operations. The number of workmen required for one hearth per shift is: One Mabuki man, one helper, one boy (for a few hearths).

SMELTING PLANTS BELONGING TO THE FURUKAWA CO.

The Ashio Smeltery.

Location.—The smeltery of the Ashio Copper Mines is in the town Ashio, about 13 miles from Nikko.

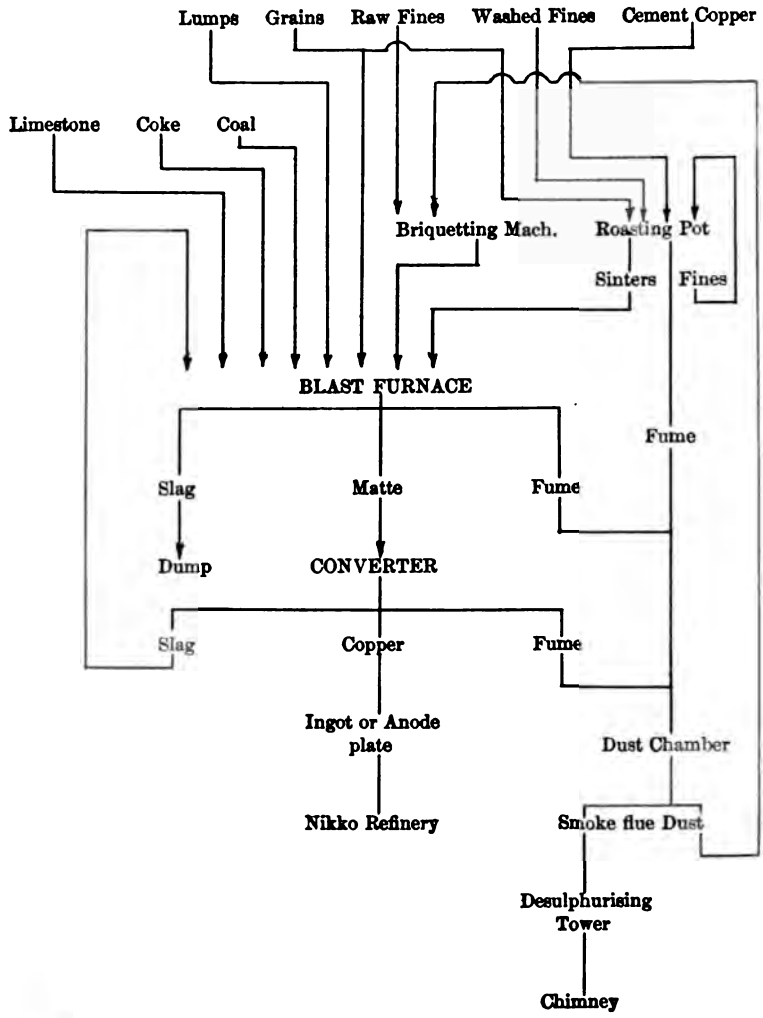
History.—The mines were discovered in 1609 and copper was produced in 1611. After it had passed through many ups and downs it finally came into the possession of the late Ichibei Furukawa in 1877. but in such a poor condition that the production was only 52 tons of copper a year. By his and his successors' vigorous efforts and careful administration, the mines were brought into such a prosperous condition that the production of copper now amounts to 11,000 tons a year.

Ores.—The ores consist chiefly of chalcopyrite, pyrite, quartz and a little of zinc-blende and galena. The ore as received is sized into three classes: viz., lumps, grains, and fines. Cement copper is also treated. About 111,000 tons of ore are smelted annually, having an average copper content of 11.50% and about 11,000 tons of copper are produced.

Smelting Process.—The lumps are charged to the blast furnace in a raw state, and the fines in a sintered or briquetted form. The matte obtained is subjected to the Bessemer process. The process will be seen in the following schematic diagram.

Pot Roasting.—Washed fines, flue dust, etc., are agglomerated in pots. The pot used here is of a conical shape and is made of cast iron. After the sintered mass has cooled thoroughly it is crushed into suitable size by hand for charging to the blast furnaces. There are 8 pots, 4 of which are each 10-

ton capacity and four 5-ton. The charge consists of 10% of grains, 78% of washed fines, 10% of flue dust and 2.0% of cement copper. The time required for sintering is about 10 hours. The blast pressure used is 15 oz.



Briquetting.—Raw fines and flue dust are briquetted by three of our briquetting machines, for which we hold the patent in Japan. Forty-five tons of fines can be briquetted by these

three machines per day, requiring only 3 horsepower. The charge is a mixture of 70% of raw fines and 30% of flue dust. Briquettes thus obtained are charged into the blast furnaces after drying.

Smelting.—The smelting is done by four rectangular water-jacketed blast furnaces. The dimensions are as follows:

	Size at tuyère level	Diam. of tuyères	No. of tuyères	Height from centre of tuyères to feed floor
No. 1.....	180" x 42"	4½"	28	11' 3"
No. 2.....		4½"	28	11' 3"
No. 3.....		4½"	24	11' 3"
No. 4.....		6"	22	7' 7"

The capacity of the No. 1 and No. 2 furnaces is 100 tons each and 90 tons for the No. 3 furnace, while the No. 4 furnace has a much smaller capacity, same being only 55 tons per 24 hours. Each furnace, except the No. 4, has a circular settler 12 ft. in inner diameter and 4 ft. in depth, lined with magnesite brick. The No. 4 furnace has an Orford forehearth 48 in. by 32½ in. The furnaces are charged to obtain a slag of the following composition and 40% copper matte.

Composition of Slag.

Silica	36% to 38%
Lime	18% to 20%
Copper	0.20% to 0.25%
Ferrous oxide	28% to 30%
Alumina	7% to 8%

The normal charge is as follows:

Lumps	45%
Grains	7%
Briquette	24%
Sinters	24%

And moreover about 20% converter slag is added to the above ore charge, using 10% coke, 36% limestone and 3% coal to the ore charge; coal is forced into the furnace from the tuyère. The blast pressure used is 1.1 to 1.3 lbs.

A revolving cone is used for agglomerating flue dust produced from the furnace by means of converter slag.

330 tons of ore are smelted per day.

Converting.—Matte is tapped from the settler into a ladle, the capacity of which is 4 tons, and is charged to converters by means of an electric traveling crane. Three cranes, one 20 tons and two 25 tons, are employed, the span being 35 feet. The converter is of the barrel type, 72 in. by 100 in., with 11 tuyères of 1⅛ in. diameter. There are nine converter shells and three stands equipped with hydraulic tilting apparatus. The blast pressure used is 10 lbs. per sq. in. For the lining material decomposed liparite (which has no value) is used mixed with copper refinery slag, it being impossible to get metal-bearing material cheaply. The lining is done by means of a tamping machine (Ingersoll Rand D-16) actuated by compressed air at 60 lbs. per sq. in. Two endless straight-line casting machines are used, each carrying 66 moulds on it and capable of making 600 ingots of 66 lbs. an hour. Moreover, three sets of vertical anode casting moulds are in use, one anode plate weighing 400 lbs.; 70,000 lbs. of blister copper are produced per day.

Analysis of the Blister Copper.

Au	0.00031
Cu	99.057
Se and Te	0.034
As	0.029
O.	0.54
Ag	0.12233
Fe	0.052
Bi	0.006
S	0.028

Treatment of Smoke.—The smoke from 3 of the furnaces is forced into 3 Asano's Cyclone dust catchers (20 ft. diameter) by 3 centrifugal fans. Having precipitated nearly all of the suspended dust, in the chamber, the fumes enter a common flue and join with the smoke from the pots, converters and the other blast furnace; the combined smoke thence passes through a long flue, to the bottom of the desulphurising tower, wherein the sulphurous acid gas is absorbed by a shower of lime water, and the purified gas escapes through the chimney. The waste water is sent to the precipitating and filtering ponds.

The amount of smoke is 100,000 to 120,000 cu. ft. per minute. Lime water (0.2% solution by weight) used is 60 cu. ft. per minute. A new flue system to meet the requirements of the Government is now being built and will be finished by July, 1915. The flues, chamber houses and stacks are built of reinforced concrete lined with acid-proof material. After passing through Asano's separator, where a large percent of the dust is deposited, the furnace gas enters the chamber house through long inclined and horizontal flues having many hoppers. The main building of the chamber house is 220 ft. long by 100 ft. wide, so that the gas passes through with a maximum velocity of 2 ft. 10 in. Wire, as has come to be the common practice in United States, will be used in this chamber for the separation of the dust from the furnace gases. Many hoppers are equipped in the bottom of this chamber, in the first few of which the dust collected will contain copper in sufficient quantity to make it of commercial value and importance and to be subsequently recovered. In the large part of the chamber the dust will contain arsenic, zinc and other impurities that will have no value; hence, they may be discarded. The chamber is connected to four stacks, each 20 ft. diameter and 100 ft. high, three of which will be in constant use. The furnace gas after being separated from the dust, fumes and sulphuric acid, will be introduced into stacks where the gas is diluted with fresh air by means of fans, one of which is installed at each stack. This diluted gas escapes into the open air. The centre line of the stacks is perpendicular to the direction of the prevailing wind of Ashio Valley, and by this means the gas further diluted.

Blowers.—Three No. 6 Roots blowers are employed for pots. One No. 8 Roots blower is used for each of furnaces No. 1 to No. 3. For the No. 4 furnace, two No. 6 Roots blowers are used. The blast used by converters is delivered by two horizontal blowing engines electrically driven (one capable of supplying 4400 cu. ft. and the other 3000 cu. ft. of free air per minute); also by a vertical blowing engine driven by water power, the capacity of which is 3000 cu. ft. per minute.

Power.—Total power consumed in the plant is about 610 kva., which is supplied by the Hosoo hydro-electric power plant near Nikko and 13 miles from Ashio.

Transportation.—All materials, coke, limestone, copper. etc., are transported by means of the Ashio Railway.

For the transportation of the blast furnace slag to dump, the Tamamura aerial ropeway, 1.6 miles long, is employed, 27 tons of slag being transported per hour.

Workmen.—Three hundred and sixty-five labourers are employed, working two shifts of 12 hours each.

The Ani Smeltery.

Location.—The smeltery of the Ani copper mines is in the town of Ani in Akita prefecture.

History.—The mines were discovered in the latter part of the seventeenth century. At the end of the nineteenth century the mines were worked on a large scale under the direction of European engineers.

Ores.—The ores treated are chiefly chalcopyrite, associated with quartz and iron pyrite at the rate of 48% silica, 8% copper, 18% iron and 17% sulphur on the average. About 18,800 tons of ores are treated annually and produce 1400 tons of copper.

Smelting Process.—Washed fines and slimes are agglomerated by the pot roasting process. Raw fines are briquetted by a briquetting machine similar to those used at Ashio Smeltery. The ores thus obtained are charged to the blast furnace together with raw lumps, limestone and coke. The resulting matte is blown into blister copper by the "Mabuki" process.

Pot Roasting.—Four pots are installed, each 6 ft. 6 in. diameter, 5 ft. deep and of 6 tons capacity. Three of the pots are always in use. The blast pressure is 12 oz.

Briquetting.—One briquetting machine is in use, treating a mixture of raw fines and flue dust.

Smelting.—There are two furnaces, same being used alternatively, the dimensions of which are as follows:

Size at tuyère level	Diam. of tuyères	No. of tuyères	Height from centre of tuyères to feed floor
8′ x 3′	4½″	10	11′ 3″
5′ 6″ x 3′	3″	7	11′ 3″

Seventy-seven tons of ore are smelted and 11 tons of 47% copper matte are produced, the slag containing 44% of silica—the copper content of the slag being 0.35%.

Converting.—Seven Mabuki hearths, each 3 ft. 3 in. diameter and 1 ft. 1 in. deep, are used to convert the matte, producing 110 to 120 tons of copper, 98.6% in purity, per month. The blast pressure is 12 oz.

Blowers.—Three No. 6 Roots blowers are employed for the use of the pots, the blast furnaces and the Mabuki hearths.

Workmen.—One hundred and forty labourers are employed, working in two shifts of 12 hours each.

COPPER WORKS BELONGING TO THE FURUKAWA CO.

History.

The electrolytic copper refinery of the Furukawa Co. originated with a small experimental plant in the Honjo Copper Works, Tokyo, in 1884. In 1891, the experiment was carried out commercially on a small scale, adopting the multiple system with a dynamo of 20 volts and 240 amperes. A wire mill was added to the plant in 1897. Shortly after, the works were enlarged to the capacity of 160,000 lbs. of cathode copper per month, current density being 9 amperes per sq. ft. A few years later there was an increased demand for copper wire and a new refinery and a wire mill were erected near Nikko. The series system was adopted with a current density of 27 amperes per sq. ft., the generator being of 180 kw. Afterwards, the plant was doubled and the current density was brought down to 20 amperes per sq. ft. The total output then became 1,800,000 lbs. per month. In 1912, a multiple plant of the capacity of 900,000 lbs. of cathode copper per month at a current density of 18 amperes per sq. ft. was also added, with a dynamo delivering 5000 amperes at 60 volts.

Electrolytic Plant in the Honjo Copper Works, Tokyo.

The multiple plant as opened in 1891 at the Honjo Copper Works was equipped with the following apparatus:

One Wolff's 8½-hp. portable locomotive type boiler, with a single-cylinder engine; 1 Siemens 4.8-kw., 20-volt, 240-ampere, shunt-wound direct-current dynamo; 42 six-pound, lead-lined wooden electrolytic tanks, 69 in. by 43 in. by 30 in.; 3 lead-

lined reservoirs, 60 in. by 60 in. by 36 in.; 1 lead-lined acid pump with rubber membrane.

The tanks were arranged in 4 rows as shown in Fig. 1 herewith, and the shape of the anode was as shown in Fig. 2 herewith. The distance from centre to centre of cathode hangers was 6 inches. The voltage of each tank was about 0.45 volt in spite of a very low current density, as the plant was provided with no heating apparatus. The multiple plant opened in 1898 was equipped with: One Siemens dynamo, 35 kw. (1000 amperes, 35 volts); 1 Miyoshi's dynamo, 35 kw. (1000 amperes, 35 volts); 78 lead-lined, wooden tanks, 1560 mm. by 900 mm. by 1000 mm.; 1 Wolff's 100-hp. cross-compound condensing engine; 1 Enke blower, 80 mm. mercury column; 2 Roots' water-tube boilers, each with a heating surface of 825 sq. ft. The tanks were all on the same level; electric connection was the same as in the old plant. The circulation of electrolyte was done individually for each tank by blowing air in one side of the tank, and the heating was done by a steam pipe at the other side. This method was, however, incapable of maintaining a uniform composition of electrolyte throughout the plant, and was replaced by the cascade system.

The anode was of the lug type (5.5 sq. ft.) and each tank had 9 anodes. These works were closed in 1908, a large portion of the equipment being moved to the Nikko Works, which had been opened in 1907.

The Nikko Copper Works.

The cost of power in Tokyo was moderate at the time when Iwaki dust coal was used as fuel. The price of coal advanced after the Chino-Japanese war on account of the increased demands. At this time, Nikko, where water power was easily obtainable, was selected as the place for the new works. After careful investigation, the series process was adopted for the reason that if the copper refined by the reverberatory furnace was used as anode, the series system was much more preferable than the multiple process where interest is high and wages are low, as is the case in Japan.

The current density first adopted was 27 amperes per sq. ft., on account of the low cost of power in Nikko, but it was later reduced to 20 amperes.

This plant is now producing 1,800,000 lbs. of refined copper per month. In the extended electrolytic plant completed in 1912 the multiple process was adopted, the reasons being: first,

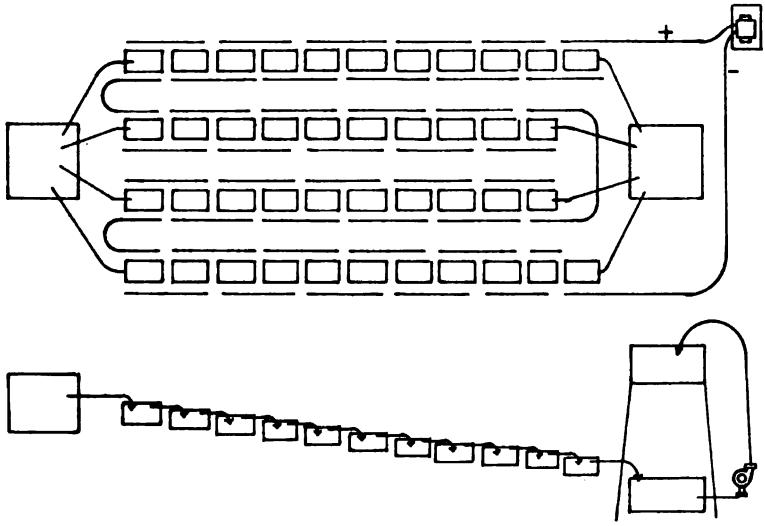


Fig. 1.

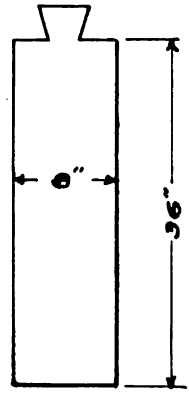


Fig. 2.

the possibility of making converter anodes in the Ashio smeltery; secondly, facilities for heavy transportation over the Nikko electric railway and the Ashio railway recently opened; and, thirdly, the expensiveness of coal. This plant is now produc-

ing 900,000 lbs. monthly at a current density of 18 amperes per sq. ft., and has ground reserved for a future extension for doubling the production.

(a) The Series Process.—The electrodes used are rolled sheets, each having the following dimensions:

Length, 24″; width, 12″; thickness, ¼″.

Average composition is:

Cu 99.4%, Ag 0.13%, Au 0.0004%.

The blister copper after being treated in a reverberatory furnace is cast into cakes two feet long, one foot wide and two inches thick. These cakes are reheated in the reheating furnaces, then rolled by a two-high roll, sheared, straightened and then sent to the electrolytic tank room. The electrolytic tanks are made of wood and doubly lined with asphalt and have two compartments, each compartment being capable of receiving 84 pieces of electrode, so as to make 42 poles. The tanks are arranged as shown in Fig. 3 herewith, twelve tanks to a section. The electric connection is seen in that sketch, each row, i. e., α, β, γ and δ, having an individual ammeter. The electrolyte comes from one head tank to each row and returns to one receiving tank, and is pumped up again to the head tank by means of an air lift pump. The potential difference between A section and N section is more than 200 volts, so that it is necessary to insulate the electrolyte by inserting an insulating vase in the inlet and the outlet of each of the rows.

The construction of a vase is shown in Fig. 4 herewith—a lead tray having numerous hemispherical projections in its bottom, each projection having one small hole 1-16 in. diameter. The electrolyte falls down through those holes in drops and is completely insulated. All the electrolytic tanks are made of wood and have ½-in. asphalt lining. The temperature of the electrolyte is kept at 100° F. and it contains 35 grams of copper and 100 grams of sulphuric acid to a litre.

(b) Multiple Process.—Anodes are directly cast from converters at the Ashio smeltery. The size of the anode is 2½ ft. by 3 ft. by 1½ in. and it contains 99.1% copper, 0.0003% gold, 0.1% silver.

Each tank contains 20 anodes and 21 cathodes. The area of the cathodes is a little larger than that of the anodes. The distance from centre to centre of the anode is 5½ in. The

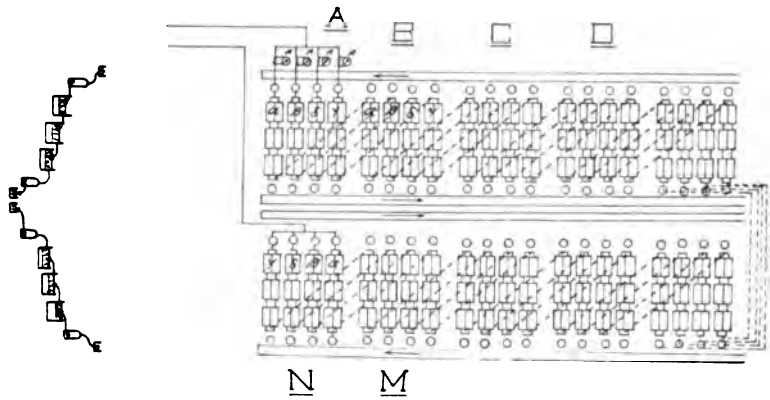


Fig. 3.

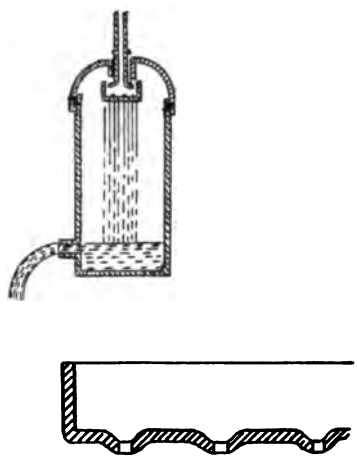


Fig. 4.

arrangement of the tanks is after the Walker system and the plant has 12 rows, as shown in Fig. 5 herewith. The tank room is constructed of reinforced concrete after the Kahn system and is equipped with a Whiting 5-ton anode handling crane.

(c) Bluestone and Slime Treatment.—Both the series plant and the multiple plant have acid recovering tanks and bluestone plants for purifying their electrolytes. The evaporating furnace, shown in Fig. 6 herewith, is directly heated by burning wood or coal; the kettle is an inclined shallow rectangular one made of sheet lead and has a corrugated bottom, so that the solution first enters the topmost furrow, then flows over the ridge to the next furrow and so on. Thus the descending solution is discharged from the lowest furrow, which is the largest and is just above the fire place. The solution is delivered, losing its half volume, while it is descending 18 ft. The concentrated solution is poured into the crystallizing tanks and stands for a few days. In the slime house, the slime is first treated in a centrifugal filtering machine and then roasted in a pot; the issuing gas is washed by water before it goes to the chimney. The roasted slime is mixed with lead and sent to the cupelling furnace to obtain noble bullion. Moreover, the plant has a reduction furnace and a liquidation furnace.

(d) Power.—The power for the series process is supplied from two generators, both directly connected to water wheels, and each yields 600 amperes at 300 volts. The power house is close to the tank house. The power for the multiple process is supplied from a motor-generator, the capacity of which is 300 kw. The direct-current generator delivers 5000 amperes at 60 volts, and is coupled to a synchronous motor of 3000 volts, which is driven by current from one of the large generators at the Hosoo hydro-electric plant, one mile distant from the tank house.

(e) Reverberatory Furnaces.—There are four reverberatory furnaces, the capacity of each of which is 70,000 to 100,000 pounds per charge. The flues of two of them are connected to a 150-hp. Stirling boiler, in order to utilize the waste heat. There are two kinds of casting machines—one is the ring system, casting cakes for the electrodes, the other is the movable launder system for wire bars and ingots.

Copper Wire Industry in the Nikko Works.

The copper wire industry of the Furukawa Co. was originated at the Honjo Copper Works, where a three-high roll, a

finishing train, and 40 single drawing machines were installed in 1897. This factory was transferred in 1908 to the Nikko works, which were opened in 1907. The Nikko works consist of

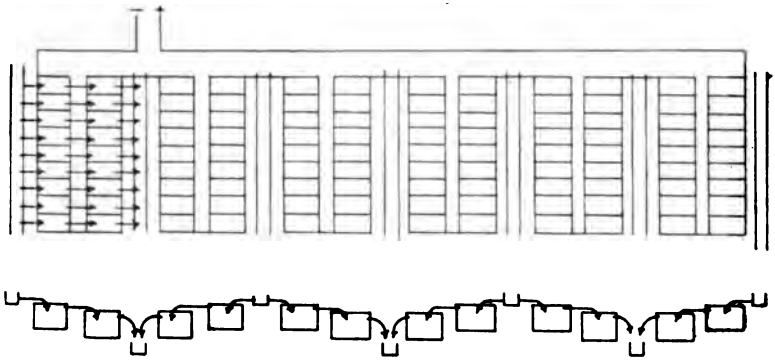


Fig. 5.

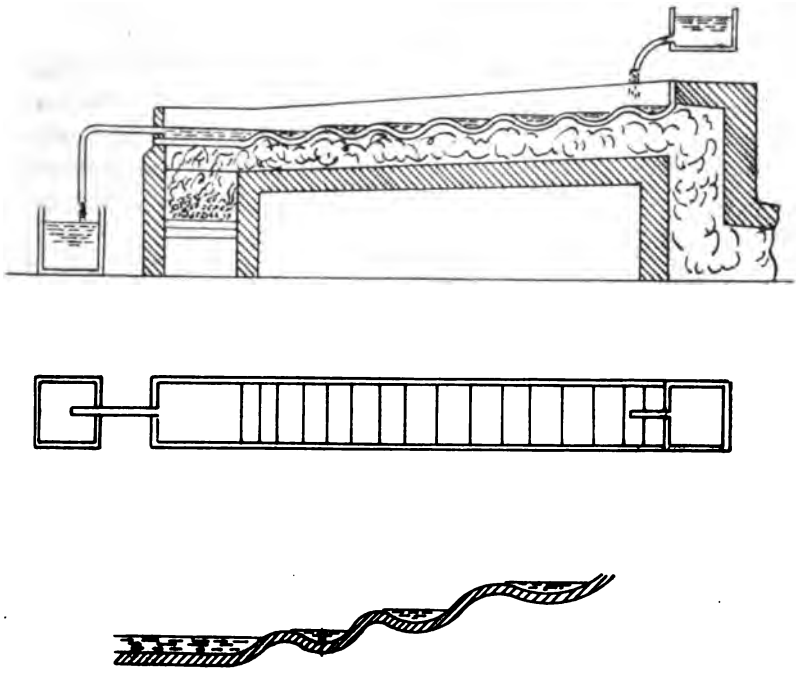


Fig. 6.

a rolling-mill house, drawing-mill house, copper-ribbon house, and annealing-furnace house. In the rolling-mill house, there are one set of three-high cogging rolls, the intermediate rolls and the finishing trains; they are all driven by a 600-hp. water turbine. In the drawing-mill house, there are 15 tandem drawing machines, 50 single blocks and two trolley-wire machines. In the copper-ribbon house, there are two cogging rolls, two finishing rolls and six copper-bar draw benches. In the annealing-furnace house, there are two Bates and Peard annealing furnaces. These works produce 2,700,000 lbs. of copper manufactures per month.

Electrolytic Plants of Other Companies.

There are four electrolytic plants running in this country besides the Nikko works, namely, the Kosaka smeltery, the Hidachi smeltery, the Mitsubishi refinery at Osaka and the Osaka Electrolytic Copper Refining Co., all having adopted the multiple system. The newest of these plants is that of the Hidachi smeltery, the electrolytic tanks therein being arranged after the Walker system.

The monthly productions are 1,600,000 lbs. in the Kosaka smeltery; 2,400,000 lbs. in the Hidachi smeltery; 2,200,000 lbs. in the Mitsubishi refinery at Osaka and 530,000 lbs. in the Osaka Electrolytic Copper Refining Co.; thus the total annual production of electrolytic copper in Japan, including Nikko, is about 57,000 tons.

DISCUSSION

Mr. Read.

Mr. T. T. Read,* Mem. Am. Inst. M. E., stated that the paper in question was a discussion of the practice at the Furukawa plant, which is very old and the pioneer plant of Japan, rather than a treatise upon the metallurgy of copper in Japan as a whole. In Japan the smelter fume problem is of even more importance than in the United States, on account of the dense population and the particularly harmful effect of sulphur dioxide fume upon the rice crop at certain seasons, when smelters are required to run low and even at times to entirely shut down. This, he said, held true of the Furukawa plant, although it is situated in the mountains. In order to protect the forests and the hillside willows, the government also required effective treatment of the fume. For this purpose, the process of neutralizing the sulphur dioxide fume with lime water is in use at Ashio. It is rendered possible here through the cheap labor which can be had in Japan.

* New York, N. Y.

Paper No. 184

SYMPOSIUM ON THE CYANIDE PROCESS.

Edited by

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COARSE CRUSHING PLANT; 1,000 TONS CAPACITY.

By

G. O. BRADLEY,
Mechanical Engineer,
San Francisco, Calif., U. S. A.

In recent years the equipment and arrangement of crushing plants are receiving the same careful study and attention on the part of mill men and engineers that are devoted to the other departments of the modern reduction works, and this general awakening of interest is very evident from the fact that we now have in operation many efficient crushing installations which balance very favorably with the other departments in the point of economical performance. We have passed beyond the age of grossly light and inefficient apparatus for this important work, and one can plainly see the results reflected in the cost sheets of our up-to-date crushing installations.

We now have on the market various types of crushing machinery, which have been developed and perfected after years of experience, and we are indebted in a very marked degree to the manufacturer for the efficiency of our modern crushing machines, as they have willingly supported us with their own engineering skill, as well as liberality, in the replacing of machine parts that may have proven inefficient or not suited to the service required. Today, the engineer has at his command a most complete line of primary-crushing and coarse-grinding machinery, and in my opinion, the following classifi-

cation may safely be followed in making the proper selection of a primary crusher that will give the best results on a given ore:

Character of Ore	Type of Crusher Recommended
1. A hard, tough, sharp-breaking rock.	(a) Gyratory Crusher.
	(b) Jaw Crusher.
	(c) Edison Rolls Crusher.
2. Medium-breaking ore.	(a) Gyratory Crusher.
	(b) Jaw Crusher.
	(c) Fairmount Crusher.
	(d) Edison Rolls.
3. Soft, easy-breaking, clayey ore.	(a) Fairmount Crusher.
	(b) Edison Rolls.

Note: The Fairmount crusher is a new development in primary crushing machinery, and its design is along the lines of a compromise between the Edison rolls and the jaw crusher, in that it has a single segmental jaw and a single revolving hub or core, into which are inserted manganese-steel breaking lugs or knobules. The jaw is held up to the work by means of massive tension rods.

It resolves itself, therefore, upon the engineer to select the apparatus best adapted to the particular problem that he is to deal with. It is, of course, important that he should have in his possession all the governing data relative to the plant requirements and the character of ore to be treated, and in this connection I have outlined the principal subjects of information for the general guidance of the designer, which are as follows:

1. The system of mining employed. This can be divided into two classes, viz.:

(a) Surface Mining
(b) Underground Mining

2. The capacity of plant per hour in tons, and the uniformity of the finished product.

3. Nature of the material to be crushed—degree of hardness and moisture characteristics.

4. The proper location of the plant in its relation to the other departments.

5. Mechanical efficiency, accessibility to all working parts of the machinery, and the economy of operation.

6. The type of power available.
7. Class and type of construction.
8. Lighting, heating and ventilation.

Surface mining requires, as a rule, massive equipment for primary crushing, for the reason that it is necessary to rough down the large pieces of rock too cumbersome to be handled economically within the limits of a finishing plant; therefore, in the case of steam shovel or surface mining, the gyratory crushers shown should be preceded with a primary crushing or roughing plant.

The arrangement of the plant selected to accompany this discussion is illustrated by the accompanying drawings, Plates I, II, III and IV, and the design is offered with a view of answering the general requirements of coarse crushing as applied to any system of underground mining where it is desired to produce a finished product for subsequent milling operations. In the selection of the design, I have been governed by the following general conditions.

Flow Sheet: The primary ore to be delivered to the crushing plant at the receiving point above the grizzly screens, or it can very conveniently be delivered directly into the coarse-ore bin, as shown on Plate III under notation, "Alternative delivery point for the coarse ore".

The ore is fed from the bin into the gyratory crushers, which, after crushing, discharge into the receiving pockets, from which it is elevated by means of the automatic skips and discharged over the sizing grizzly.

The oversize returns to the coarse bin by gravity for re-crushing, and is retained in this closed circuit until it is fine enough to pass the sizing grizzly. The undersize is fed onto the undersize conveyor by revolving drum-type feeders and is conveyed to the fine ore bin, more plainly shown on Plates I and II.

From this point, the ore is uniformly fed over the dry impact screens, and the oversize is collected on the lateral conveyors which discharge into the 54 in. by 20 in. rolls.

The undersize from the impact screens is discharged onto the conveyor for the finished product, as indicated more clearly on Plate II.

The ore, after passing the rolls, falls by gravity into the receiving pockets, and is charged automatically into the skips and returned to the fine ore bin, where the above process is repeated until the ore is reduced sufficiently to pass the ¼-in. mesh screens.

Type of Plant: Dry crushing.

Capacity: 1000 tons per day.

Material: Ore of average hardness, and such as produced by the present practice of underground mining.

Equipment: Arranged for graded crushing and rolling, with oversize return.

Product: Finishing to pass through ¼-in. mesh screen.

Power: Electricity.

Construction: Concrete and steel throughout.

A general description of the equipment to be in accordance with the following discussion under their respective subheadings:

Building: The building to be of concrete and steel construction throughout, having the coarse and fine ore bins in alignment at the head of the mill, and arranged for electric crane-way over the entire operating floor. All crushing machinery and auxiliary apparatus to be installed on a single level, so as to minimize attendance and facilitate maintenance and repairs. The fine-ore bin to be constructed with the suspended-type steel bottom, which is more clearly illustrated on Plate II.

Crushers: The crushers contemplated for this installation are two No. 7 gyratory type, standard discharge, set to crush 2½-in. ring gauge.

Feeders: Each crusher is fed by an individual drum-type revolving feeder, located at the side of the coarse ore bin. The feeders are provided with proper feeder housing and hand-operated geared cut-off gates between same and the ore supply. The feeders are driven from the crusher pinion shaft, thus insuring, automatically, a stoppage of feed when any one of the crushing units is not in operation.

Rolls: The 54-in. diameter by 20-in. face rolls proposed for this installation are of the heavy-pattern self-contained type. In each case the stationary rigid-roll shaft is provided with out-

board bearing. The driving pulleys are both mounted on the same side, in order to give a much greater factor of safety and freer access to the operator when making repairs or inspection of the running machines. The rolls are designed for a combined working load or spring capacity of 15,000-pounds pressure per inch of width on the roll face. The main driving pulley for each set of rolls is of the heavy fly-wheel type, 108-in. finished diameter by 17-in. crown face. The hubs and rims are of cast steel, and the center is formed by two steel web plates ½-in. in thickness and dished so as to give lateral stiffness. These plates are riveted to the hub and rim castings by machine-turned through rivets. The approximate weight of each pulley is eight tons. This heavy fly-wheel has the effect of producing a very steady and smooth running unit, and increases the efficiency very materially.

Feeders: The undersize ore is fed from the fine-ore bins by revolving or drum-type feeders, illustrated in section on Plates I and II and in plan on Section BB, Plate I. The ore is fed uniformly over the impact screens, where the oversize is collected onto the belt conveyor feeder, which carries same to the roll units. The undersize or finished product is collected by the branch launders and delivered onto the conveyor, where it is transported to the sampling and fine grinding departments for further treatment.

Drives: The conveyors, feeders, and screen drives are taken from the roll shaft, as it will be noted that each set of rolls is provided with an independent nest of feeders and screens. The main drives consist of two 150-hp. motors of the double-end type, having a flexible coupling connecting the transmission shafts at each end, also a friction coupling or cut-off which enables the operator to run any machine independently or together as may be desired. This system of drives applies to both the crushers and rolls, as is clearly shown in Plates I, II and III.

Automatic Skips: The crusher and roll units are each provided with balanced automatic skips in place of the ordinary belt elevators commonly used for this class of work, and the advantages of the skip over the belt elevator are numerous. The skips are more wieldy and can operate to any height de-

sired, making it possible to concentrate the equipment and operating labor, at the same time avoiding all the annoying evils so prevalent in connection with belt elevators.

The operation of the balanced automatic skips will be in accordance with the following general description:

The arrangement of the loading apparatus at the bottom of the shaft is such that when the empty skip comes into place it engages the automatic-skip loading-mechanism, which closes gate "U" completely; then gate "R" starts to open. The measuring hopper holds, when filled, one skip load. As the weight of the load increases, the loaded skip compresses the weighted platform at the bottom of the shaft, overcoming the resistance of counter-weight "T". This movement is sufficient to trip the lever operating a master controller, and which automatically starts the hoist. As skip "B" starts to ascend, the engaging mechanism follows with it, due to the over-balancing of counter-weight "S". The first cycle closes gate "R" completely, and as the skip continues on its upward movement gate "U" opens and remains in this position until the skip returns on its downward travel.

A geared limit switch of the traveling-nut type is mounted on the hoist and so arranged as to allow the hoist to coast momentarily when either of the skips approaches the dumping position. Just before the skip reaches its proper limit of travel, the limit switch will automatically de-energize the solenoid brake, thus bringing the hoist to rest. Hatchway limit switches are also located in such a manner as to be operated by the motion of the skip itself. These hatchway limit switches will serve as an additional precaution in case of failure of operations of the geared limit switch. The master controller is also inter-connected by means of a double-throw knife switch, so that hand operation may be obtained at the will of the operator. The automatic master controller will have only three points, i. e., a neutral position at the center of throw and a position on each side of the center for either direction of hoisting.

The method of the operation and control will be as follows:

Assume that skip "A" is being hoisted and skip "B" being lowered. Just before the skip "A" reaches the dumping point, the hoist will be slowed down by gravity to approxi-

mately half-speed. When skip "A" has reached a point perhaps two feet from its final position, skip "B" will engage with the scale platform, depressing the latter for a short distance and increasing the load upon the motor by increasing the unbalanced effect of the upper skip. When skip "A" reaches its final limit of travel, the solenoid brake will be applied by means of the limit switch. Skip "B", however, will have to come to a standstill in the meantime, so that there will be a small amount of slack in the "B" cable. The ore now being dumped into skip "B" will cause a further depression of the platform and a movement of one of the operating arms attached to the automatic master. The latter, which has been in the proper position for hoisting skip "A", will have its handle pushed past the neutral position and into the position for hoisting skip "B"; it will be held in place by a roller falling into a notch on a star wheel. Since the limit switch will offer no opposition to hoisting skip "B", the latter will now start to rise. Retardation will then take place when skip "B" reaches the upper end of its travel, as previously described in the case of skip "A".

	Estimated Cost.	
Building:		
Grading	$ 2,000	
Concrete	6,000	
Steel, building	31,500	
Steel, corrugated	2,085	
Sheathing and Nailing Strips	900	
Doors and Windows	1,600	
Floors	360	
Grizzlies	385	
Stairs	750	
Lighting and Wiring	2,300	
Laundering	300	
Crane	4,000	
Painting	800	$ 52,980
Equipment:		
2 No. 8 Crushers	8,100	
Freight, at $1.50 per 100 lb.	3,045	
Erection, " " " "	3,045	
2 Gates and Special Chutes	90	
4 Feeders	500	
12 Feeders	1,500	
12 Impact Screens	2,760	
2 54" x 20" Rolls	10,650	
Freight, at $1.50 per 100 lb.	3,803	
Erection	2,500	
2 Automatic Hoists, complete	13,800	
4 Loaders	1,680	
2 150-hp. Motors and Starters	3,900	
Complete Transmission, Belting, Etc.	2,900	
Complete Conveyors and Drives	1,050	59,323
		112,303
Miscellaneous and Supervision, 5%		5,615
Total Estimated Cost		**$117,918**

DISCUSSION

Mr. Lachmund.

Mr. Oscar Lachmund,* Mem. Am. Inst. M. E., asked if it were true that jaw crushers delivered a more uniform product than gyratory crushers.

Mr. DuRell.

Mr. C. T. DuRell.† Mem. Am. Inst. M. E., said that he considered the whole question as being one of relative economy of operation of the two types of crushers.

Prof. Hersam.

Prof. E. A. Hersam,‡ Mem. Am. Inst. M. E., stated that he thought there was little difference of efficiency between a reciprocating jaw crusher and a gyratory crusher, but that it might make a difference whether the power was applied below or above the fulcrum of the jaw. He, therefore, thought that it might be possible that a higher efficiency at times was realized with machines of the Blake type. He also called attention to the effect of the rapidity of impact, a question which had been much neglected in connection with rock crushing. In other words, he deemed the time factor a most important one.

Mr. Simonds.

Mr. E. H. Simonds,** Mem. Am. Inst. M. E., stated that some years ago it was considered good practice to install a large jaw crusher in order to do away with the sledging of the large boulders which is necessary when a gyratory crusher of equivalent capacity is used. On the whole, he thought that, aside from this, the gyratory crusher presented certain advantages. He also called attention to the fact that Mr. Bradley had not mentioned in his paper the disc pulverizers, which are now coming very generally into use.

Prof. Clevenger.

Prof. G. H. Clevenger,*** Mem. Am. Inst. M. E., stated that it is no longer true that the large sizes of gyratory breakers do not take the largest boulders coming from the mine.

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Paper No. 185

CRUSHING AND GRINDING.

By

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PRIMARY CRUSHING.

In the first paper of this series Mr. George Bradley has described a crushing plant to handle 1000 tons per day of an average ore, reducing from run-of-mine to a point where all passes 0.25 in. aperture. This combination of gyratory crushers and rolls is not at present in general use in preparing ores for cyanide treatment, but there seems little reason to doubt that it will play an important part in the preliminary crushing of the very large low-grade deposits which are rapidly assuming importance in the metallurgy of gold and silver.

Where the adjuncts of very large-scale operations are available, dry crushing with gyratory or jaw crushers, followed by rolls down to 0.2-in. aperture, stands in a class by itself, so far as costs are concerned. Such equipment is not well adapted, however, to the usual cyanide plant with limited machine shop facilities and average mill operatives. The incidental problem of dust is also one to which the cyanide metallurgist will be wisely loath to revert.

The trend of recent practice is strongly toward two-stage primary crushing, using first a large-size Blake-type or jaw crusher, located either underground or at the surface, depending on the system of mining employed, and breaking from run-of-mine to, say, 6-in. ring. This product is re-crushed in cone crushers to, say, 2-in. ring, suitable trommels or grizzlies being provided to eliminate undersize material from the feeds, but neither machine being operated in a closed circuit. Dry crushing is not usually carried beyond this point.

The Symons horizontal-shaft disc machine is a recent de-

velopment in crushing practice and is giving excellent results in breaking from 4- to 6-in. ring down to 1- or 2-in. ring, as a preliminary to further reduction in stamps, Chilean mills, or small ball mills. Undersize material should be carefully removed from the feed of this machine, either by impact screens, trommels, or inclined stationary screens (not by grizzlies). Maximum efficiency will only be obtained by operating in a closed circuit, returning the product to the eliminating screen. These crushers unquestionably have a wide range of application, particularly on hard, brittle ores, but are not adapted to wet, sticky ores or those which contain large pieces of tough schist or gouge.

As illustrating the range in cost of coarse crushing in the average cyanide plant, may be taken the figures from the 1914 Annual Reports of the four following companies, which are representative of modern American practice:

Goldfield Consolidated, Nev., crushing and conveying	$0.046
Belmont Milling Company, Nev., " " "	0.068
Commonwealth Mine, Arizona, " " "	0.079
Hollinger Gold Mines, Porcupine, " " "	0.113

FINE CRUSHING OR COARSE GRINDING.

Either of the above designations may be taken to cover the reduction of an ore from approximately 1½- or 2-in. ring to 0.25-in. aperture, depending upon whether the energy is applied by impact or attrition, or by both.

The Gravity Stamp, crushing by impact, is probably used in 95% of the cyanide plants throughout the world. Much has been written and more has been said of the faults of this machine; in particular, the high installation cost, especially in foundations and bin construction, the low power efficiency, and last but by no means least, the excessive noise. And most operators will testify that its sins have not been exaggerated. But in spite of all this it has also some most excellent virtues, inasmuch as it will crush any kind of ore from clay to chert and can be adapted to any size unit construction. Also men skilled in the operation of stamps may be found in every mining district of the world, although even this point is not vital, since the machine is so nearly fool-proof.

There is, however, at the present time, a decided tendency in American and Canadian practice to supplant the stamp with the newer types of ball mills, and it is the authors' belief that in the future, few, if any, new stamp mills will be built on the American continent. Whether this development will extend to other countries remains to be seen, but such would appear to be the logical outcome of the excellent results now being obtained.

The practice of crushing with stamps to a finished product for cyanide treatment has now become obsolete, except in a very few instances. Even the strongest adherents to stamps now admit that the final reduction should be made in some type of attrition mill, irrespective of the ultimate fineness desired.

Excepting only the increase in weight and the strengthening of individual parts to meet this increase, the gravity stamp as built today differs little from the California practice of thirty years ago. Concrete mortar blocks have replaced the former timber pile foundations, and the battery framing is, of necessity, much heavier and stiffer to stand the excessive vibration of a falling weight varying from 1250 to 2000 lbs.

The economic limit of battery screen aperture in modern plants is now considered to range from 0.15 to 0.4 in. This statement will apply either to the so-called "all-slime practice" [70% or more through 200 mesh, (0.0029 in.)] in America and Mexico, or to the comparatively coarse grinding [95% through 65 mesh, (0.0082 in.)] obtained upon the Rand.

Stamp-mill practice has reached its highest development in the Transvaal, and this is a logical result, when one considers the magnitude of operations within the limited area and the keen rivalry existing between the men in charge of the operations of the various groups. Also the assured life of the plants amply justifies large capital expenditures to obtain low operating and maintenance charges. Since the introduction of the tube mill, stamps have increased in weight up to 2000 lbs. each, but at this point the economic limit seems certainly to have been reached, and many prominent metallurgists hold to the view that, all things considered, the practical limit for a five-stamp [illegible]ut 1600 lbs. falling weight.

[illegible]e carried out in one of the

Rand plants to compare the work of the standard five-stamp battery and the Nissen, or single-unit stamp. These trials are said to have shown one-third greater capacity per pound of falling weight, and an equal gain in efficiency, in favor of the single-unit type. It is, however, significant that of the six new plants built on the Rand since these trials were made, only one proposes to make use of the new type.

The cost of stamp milling on the Rand naturally varies between wide limits, depending chiefly upon the tonnage crushed and upon the ratio of stamps to tube mills. In the modern plants, the total charge against stamp milling does not exceed 20c. per ton crushed, and the mills built within the last year are probably even a little under this figure, a truly remarkable result when one considers that the Rand banket is probably the hardest gold ore milled anywhere in the world. The average cost is, of course, above these figures, being, in 1913, 29.3 cents for thirty of the larger plants.

The following table gives the essential data of American stamp-milling practice, under widely varying conditions, both in the nature of the ore handled and the tonnage milled:

Table I. Stamp Milling Data.

PLANT	Tons Milled 24 Hours	Number of Stamps	Running Weight	Discharge Aperture	H. P. Hours P. T. Milled	Stamping Cost. Cts. P. T. Milled	Sizing	
							% —100 (0.0055 in.)	% —200 (0.0029 in.)
Mexico Silver Mill	1000	60	1450	0.371	4.8	10.0	.....	14.0
Nipissing	245	40	1450	0.334	12.1	23.8	20.3	16.7
Belmont	500	60	1200	0.131	7.2	20.7	28.3	19.5
Silver Peak	500	120	1050	0.023	13.8	31.4	54.0	40.0
Homestake	4500	1020	850	0.022	11.0	20.4	80.0	60.0
Hollinger	585	60	1400	0.263	8.6	16.0	.....	15.0
Porcupine Crown	150	20	1000	0.250	6.0	14.0	.....	15.0
Liberty Bell	485	80	750	0.041	7.8	19.1	54.0	46.0

FINE GRINDING.

The use of tube mills for final grinding to a finished product has now become almost universal in modern plants, whether for combined sand leaching and slime treatment, or for all-slime practice.

The classification or elimination of the finished products from the tube-mill feed has received particular attention and is recognized as vital for maximum efficiency. Cone classifiers, provided with diaphragms a few inches above the apex, are preferred where coarse grinding—say all to pass 65 mesh (0.0082 in.)—is employed. This classifier has been developed on the Rand, and is universally used there with most excellent results.

In America, the general practice is to use mechanical drag classifiers of the Dorr, Akins, Esperanza or Ovoca types; with the closed circuit generally used, the tube mills discharge directly into the mechanical classifier, which not only effects the classification, but also elevates the oversize back to the tube-mill scoop feed.

The efficiency of a closed circuit in tube-mill grinding has been recently questioned in the technical press, but this contention is not borne out in practice; for not only is the principle almost universally used in tube milling, but it is also extending to other grinding and crushing machines—notably ball mills, rolls, disc crushers, and even cone crushers.

Until quite recently, 38 to 40% moisture has been generally accepted as correct for the tube-mill feed, and this is probably true in so far as it applies to tube mills discharging within 6 in. of the central axis. With the introduction of peripheral-discharge mills, however, much higher moistures will undoubtedly be found advisable, particularly for coarse grinding.

The theory of this new discharge, together with the companion problems of speed and moisture, are thoughtfully discussed in a recent paper by Mr. H. A. White—Bibliography (3),—and a careful study of his conclusions is recommended to those interested in the economics of tube milling. In particular, his proposal to operate the tubes at sufficient speed to maintain an automatically renewed lining of pebbles, brings up a most interesting line of thought, especially since the diameters of tube mills have already been increased to 8 and 10 ft. in American practice, thus approaching the required peripheral speed to accomplish this result.

The proportion of tube-mill capacity to stamp capacity has gradually increased, until some of the new mills have as high as 4 cu. ft. of grinding volume for each 100 lbs. of running stamp weight. There is practically unanimous agreement that crushing and grinding costs have decreased substantially as more work has been thrown upon the tube mill, and a careful study of recent ball-mill practice leads the authors to conclude that some form of tube mill, or probably two mills in series, will ultimately eliminate the stamp.

The increasing difficulties experienced in obtaining satisfactory flint pebbles for grinding purposes have led to many independent investigations of the possibilities of steel or iron balls as substitutes. Hollow cast balls have been suggested and would seem to be logical for fine grinding, if practical to cast. Special polyhedron shapes are also being tried, with a view to reducing the interstitial spaces.

At one large mill in Northern Ontario, solid cast-steel balls up to 1½ in. diameter are being tried on a working scale, and, from results so far obtained, give promise of increasing capacity considerably in excess of the corresponding increase in power consumption, the latter being approximately 30 to 40%. It may be noted here that finely disseminated iron is no longer considered a serious detriment in cyanide treatment, and in any case, automatic electro-magnets will effectually remove the greater portion, if desired.

Another departure from standard tube-mill practice is the Marathon, or rod-mill. Iron or steel rods, from 1 in. to 2 in. in diameter, are substituted for the usual balls or pebbles, thus materially reducing the interstitial space and insuring a much more positive grinding. At a plant in Arizona, where this mill has been run parallel with Chileans and cone-end tube mills, the results so far obtained indicate the possibility of valuable results from the further development of this principle.

Tube-milling costs on the Rand have, naturally, increased in the newer plants in proportion to the altered stamp-tube mill ratio, but on the other hand, stamping costs in the same plants have decreased, the result being a net gain. Thus, newer plants show stamping and tube-milling costs to be almost equal, i. e., from 18 to 20 cents per ton milled, or a total of from 36 to 40

cents; whereas average figures from some thirty plants show stamping at 29.3 cents and tube milling at 13.0 cents, a total of 42.3 cents. And even more important than this reduction in cost is the finer grinding—[5% + 65 mesh (0.0082 in.) and 60%—200 mesh (0.0029 in.)]—and, therefore, higher extraction obtained under the new conditions.

The following table gives the essential data of tube-mill operation in various plants in America:

Table II. Tube-Milling Data.

PLANT	Tons Milled 24 Hours	No. Tubes	Dimensions of Tubes	H. P. Hours P. T. Milled	Cost P. T. Milled	Sizing Final Product	
						% —100 (0.0065 in.)	% —200 (0.0029 in.)
Mexico Silver Mill	1000	6 6	5′ x 16′ 5′ x 20′	19.2	22.0	98.0	75.0
Nipissing	245	4	6′ x 20′	44.6	50.0	100.0	100.0
Belmont	500	7	5′ x 18′	16.8	40.9	99.0	72.3
Silver Peak	500	1	5′ x 18′	2.4	2.6	64.0	50.0
Homestake	4500	2 2	5′ x 14′ 5′ x 18′	0.8	1.2	87.0	66.0
Hollinger	585	6	5′ x 20′	16.0	18.8	100.0	90.0
Porcupine Crown	150	1 1	5′ x 16′ 4′ x 20′	11.5	36.0	100.0	90.0
Liberty Bell	485	3	5′ x 22′	4.3	7.7	87.0	73.4

STAMPS, CHILEAN MILLS AND TUBE MILLS.

This system of stage crushing and grinding is used at the Goldfield Consolidated mill in Nevada, and while the practice is almost unique, the excellent costs obtained are worthy of careful study. The equipment consists of one hundred 1050-lb. stamps with 4-mesh (0.18 in.) screens, six 6-ft. Chilean mills with 30-mesh (0.012 in.) screens and six 5 ft. x 22 ft. tube mills. On a basis of 850-tons daily capacity, the following figures are obtained:

Cost Per Ton Milled.

Stamps		Chilean Mills		Tube Mills	
Labor	$0.039		$0.018		$0.014
Supplies	0.041		0.041		0.065
Power (232 hp.)	0.054	(210 hp.)	0.047	(357 hp.)	0.087
	$0.134		$0.106		$0.166

Power consumed by stamps, Chilean mills and tube mills..... 22.5 hp. hours per ton milled
Total combined cost for stamps, Chilean mills and tube mills..... $0.406 per ton milled

Sizing.

Stamp Discharge	Chilean Discharge	Final Pulp
+30.....50.0%	+30..... 4.0%	+100..... 2.6%
+100.....23.0%	+100.....25.0%	+150..... 8.1%
+200..... 7.0%	+200.....12.0%	+200..... 9.2%
—200.....20.0%	—200.....49.0%	—200.....80.1%

CHILEAN MILLS.

The use of Chilean mills following coarse- or medium-crushing rolls, to produce a final product where fine grinding is not required, while being far from general practice, nevertheless, is productive in some instances of most excellent results. The following data furnished by Mr. Crowe of the Portland Gold Mining Company will demonstrate this.

The ore crushed is of average hardness and the mill handles 690 tons per day. Coarse crushing equipment consists of one 15-in. x 30-in. Blake crusher, one 36-in. Symons disc crusher and one set of 48-in. x 20-in. rolls. Fine crushing is done by five 6-ft. Akron Chilean mills.

Roll Product		Chilean Mill Product	
+1¾" round aperture.....	0.7%	+20 (0.0250").....	5.5%
+1½" " "	2.9%	+30 (0.0166").....	10.5%
+1" " "	21.7%	+40 (0.0125").....	7.5%
+½" " "	36.3%	+60 (0.0083").....	10.3%
+¼" square "	11.2%	+100 (0.0050").....	11.2%
—¼" " "	27.2%	+200 (0.0025").....	15.0%
		—200 (0.0025").....	40.0%

The Chilean mills run at from 36 to 41 r.p.m., using from 2.5 to 3.0 tons of water per ton of ore. The Chilean steel consumption per ton of ore is 0.797 lbs. gross and 0.692 lb. net. The power consumption per ton of ore in the coarse-crushing department is 1.86 hp.-hrs., and in the Chilean mills, 13.26 hp.-hrs., or a total of 15.12 hp.-hrs.

The following cost data cover the above operations:

	Coarse Crushing	Chilean Mills	Total
Power (at 0.842c hp.-hr.)	$0.0199 per ton	$0.1118 per ton	$0.1317 per ton
Labor (operation)	0.0318 " "	0.0179 " "	0.0497 " "
Labor (repairs)	0.0103 " "	0.0039 " "	0.0142 " "
Supplies	0.0284 " "	0.0482 " "	0.0766 " "
Total	$0.0904 " "	$0.1818 " "	$0.2722 " "

BALL MILLS.

Kalgoorlie still retains the practice of dry crushing with ball mills, the two common sizes being the No. 5, 7′-6″ dia. x 3′-10″ long and the No. 8, 8′-10″ x 4′-6″, with screen areas of 70 and 100 sq. ft., speeds of 25 and 23 r.p.m., and power consumption of 25 and 60 hp. The capacity of the No. 5 is approximately 40 tons and of the No. 8, 95 tons per day, the feed being about 2½ in. and the discharge, through 28-mesh (0,020 in.) screens, is from 40 to 50% through 200-mesh (0.0029 in.). The smaller size takes about one ton of steel balls, while the larger size takes about two tons. Steel consumption per ton milled varies from 0.4 to 0.7 lbs. Average total costs of ball milling are given as $0.50 per ton milled.

Wet-crushing ball mills, following rolls or cone crushers set to deliver 1-in. or 1½-in. product and supplanting stamps, are now in operation in three cyanide plants in Northern Ontario, and with most excellent results. Steel or white cast-iron balls are used and the iron consumption is stated to be from 0.5 to 0.7 lbs. per ton crushed, a figure which compares well with stamps crushing through the same range. A visitor to one of these plants cannot fail to be impressed by the smoothness of operation and the lack of noise, but the average mill man will look with disfavor upon the return of dry-crushing roll practice.

However, there is little doubt that this combination will soon be still further simplified by the use of large-diameter wet-crushing ball mills, using steel balls 4 to 5 inches in diameter and reducing a 3-inch ring feed to a point governed largely by the requirements of the subsequent treatment. Recent tests with an 8-ft. Marcy ball mill, using ⅛-inch discharge slots,

demonstrate conclusively that, operated in closed circuit upon 4-inch ring maximum feed, the finished product may be kept under 48 mesh (0.0016 in.) if desired.

These tests showed a steel consumption of approximately 0.75 lb. per ton crushed and a power consumption of approximately 12 hp. hours per ton. Where sand leaching is to be practiced, this single-stage grinding will probably prove preferable, but if the total product is to be agitated and treated as slime, then a ball-mill product passing, say, 0.25 inch aperture and final grinding in a standard tube mill would seem a more logical arrangement.

GRIFFIN MILLS.

Originally used in Kalgoorlie in competition with ball mills for dry crushing, the Griffin mill seems to have been generally superseded by the latter. The Griffin mill runs at 200 r.p.m., and with a feed of 30 tons per day of 1½″ ore discharged through 14 mesh (0.046 in.) the final product approximates 65% through 200 mesh (0.0029 in.). The power ranges from 20 to 25 hp. Griffin mill costs run from $0.55 to $0.70 per ton milled.

GRINDING PANS.

Grinding pans were probably the strongest competitors of tube mills for fine grinding, although they are now rarely installed in new plants. Kalgoorlie has some 150 pans in use, following stamps, ball mills and Griffin mills. Careful classification, or elimination of finished product from the feed, is generally lacking in pan grinding, the usual practice being to feed the entire pulp from the preceding crushing machine. The following data represent averages of a number of installations of 5-ft. pans in Kalgoorlie. Feed per pan per day, 23 tons of sand—54% through 150 mesh (0.0041 in.). Tons of through 150-mesh material produced per pan per day, 5.4. Power per pan, 7 hp. at 55 r.p.m. Cost with power at 3c per hp. hour, per ton of feed, $0.23; per ton of through 150-mesh material produced, $0.65.

DISCUSSION

Mr. Butters. **Mr. Chas Butters,*** Mem. Am. Inst. M. E., stated that he had recently investigated the possibility of substituting steel balls for the flint pebbles generally used in tube mills. His opinion was that the flint pebbles would be displaced by the steel balls, and that with this change there would also come the practice of making the tube mills of smaller diameter and driving them at greater speed. Theoretical comparative costs which he presented for one of his properties showed considerable monetary saving in favor of the steel balls. He also said that it is evident that in out of the way places, where transportation is difficult the steel balls would be much easier to handle than the bulkier flint pebbles.

Prof. Clevenger. **Prof. G. H. Clevenger,†** Mem. Am. Inst. M. E., said that it seemed to be apparent that there would be a saving in the initial expenditure for a fine grinding plant when steel balls were used, but that he would like to ask Mr. Butters if he thought that there would be a saving in the cost per ton for grinding.

Mr. Butters. **Mr. Butters** replied that he was inclined to think that, with steel balls, higher efficiency would be realized and that the grinding costs would, therefore, be less.

Mr. Hamilton. **Mr. E. H. Hamilton,**** Mem. Am. Inst. M. E., called attention to a case with which he was familiar, where steel balls were tried for crushing coal, and the experiment proved a failure.

Mr. Merrill. **Mr. C. W. Merrill,‡** Mem. Am. Inst. M. E., thought that the difficulty in this case may have been due to the use of too small a tube, which did not permit sufficient impact of the balls.

Mr. Butters. **Mr. Butters** gave an account of an experiment which he had made with a small mill 16 in. in diameter and 14 ft. long. The efficiency of the mill appeared to depend largely upon the amount of material in the mill at any given time and overloading invariably produced unsatisfactory results.

Mr. Merrill. **Mr. Merrill** asked Mr. Butters if he thought that the steel balls would in any way cause decomposition of the cyanide solution.

Mr. Butters. **Mr. Butters** replied that he thought the effect of the steel balls on the cyanide solution would be negligible.

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Paper No. 186

SOLUTION OF GOLD AND SILVER.

By

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NOTATIONS.

U. S. currency. Tons of 2000 lbs. Assays—troy ounces per ton. Cyanide strength—lbs. of 100% KCN per ton of solution. [Protective alkalinity—lbs. of CaO per ton of solution.] Dilution, or L/S,—ratio, by weight, of liquids to solids.

CHEMISTRY.

Since the classical investigations of McLaurin, in Australia, it has been accepted that the dissolution of precious metals by an aqueous solution of an alkali metal cyanide is essentially an oxidation process, and the following so-called "Elsner equation" is generally considered as expressing the final reaction:

$$2\ Au + 4\ KCN + O + H_2O = 2\ KAu\ (CN)_2 + 2\ KOH$$

The inadequacy of this equation as a guide to consumption of cyanide is at once apparent in the treatment of complex ores, with their various constituents. The equation calls for 1.51 units of Au. or 0.83 units of Ag. per unit of KCN. With many silver ores this relation is closely approximated, but with gold ores a consumption of 20 of KCN to 1 of Au. is considered satisfactory, and 40 to 1 is more common. The earlier use of the mixed potassium cyanide salt (98 to 99% KCN) has been quite generally supplanted by sodium cyanide (120 to 129%, in terms of KCN). Subsequent references to cyanide will be in terms of 100% KCN, although sodium cyanide is used.

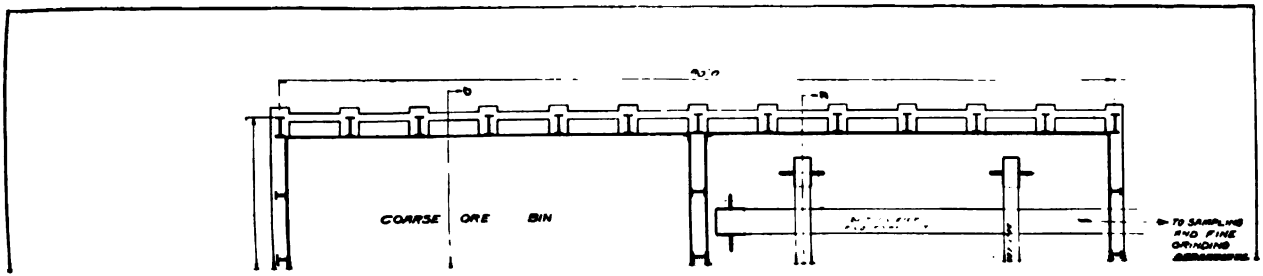
General Considerations of Solubility.

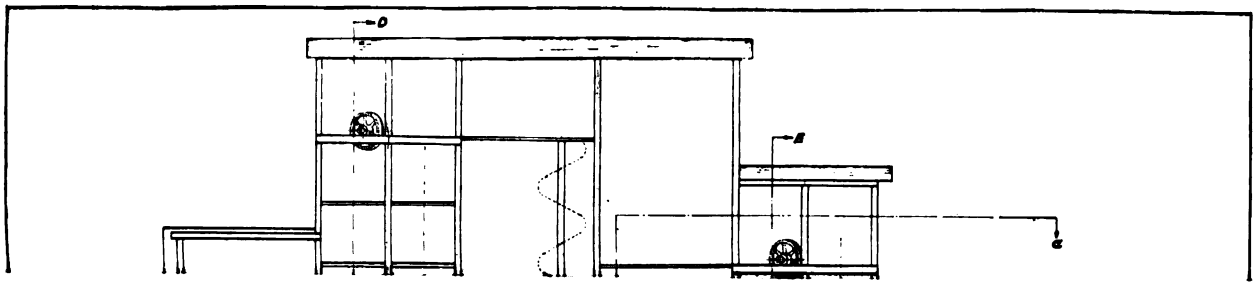
Nearly all gold and silver ores will yield to cyanide if the

precious metals can be brought into contact with the solvent, and the too excessive destruction of the solvent by other compounds of the ore be prevented. Under the physical aspect will come such considerations as the degree of pulverization, amount of metal surface exposed, presence of free gold, etc.

Chemical association with other elements which retard or prevent dissolution must be met by special preparatory treatments. The presence of oxygen-absorbing compounds demands special aeration to prevent undue consumption of cyanide and reduction in extraction. Oxidation or weathering of some of the sulphide constituents produces various acids, or free acid may exist in the ore, and proper neutralization by lime is necessary. Lime, furthermore, tends to break up certain metallic salts and form harmless hydrates, partially protects the solvent from cyanicides found in the ore, and is the most common means in assisting slime settlement by coagulation. Cyanicides, or cyanide-destroying compounds, must be removed by concentration or other preliminary treatment, while organic or other substances tending to cause premature precipitation of the precious metals must be removed, or rendered innocuous. Reducing agents, such as alkaline sulphides, frequently retard the solvent action and may cause a partial premature precipitation of the precious metals. The usual method of removing such sulphur, as an insoluble compound, is by the addition of readily soluble lead salts, such as litharge or acetate (.5 lb. per ton of ore being common), although the zinc used in the precipitation plant acts in much the same way. Numerous artificial oxidizers have given way to atmospheric aeration. It is to be noted that successful electrolytic aid in regeneration of solutions is very rare.

The strength of the cyanide solution is kept as low as conditions will allow, so as to minimize the chemical and mechanical loss, which may be estimated to average ¾ lb. for gold ores and 2 lbs. for silver ores. For the average gold ore, 1.5 lb. KCN per ton of solution, and for the average silver ore 4.0 lbs. KCN are common solution strengths. Dilutions were formerly kept at 3 or 4, but the present trend is to thicker pulp. Sand leaching plants have contacts of four to seven days, while the contact for average gold slime is, perhaps, 8 hours, and for


COARSE ORE BIN
TO SAMPLING AND FINE GRINDING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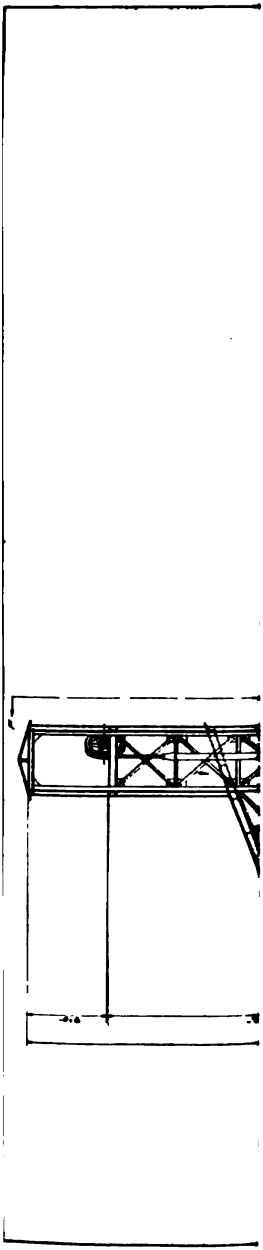

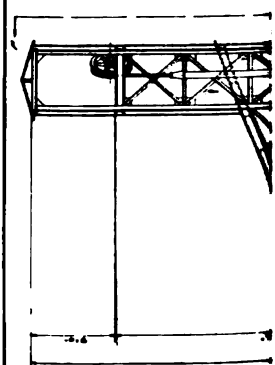

average silver slime, 48 hours. Heating of solutions has proven of decided benefit in assisting settlement, and with many silver ores, dissolution has been increased an ounce or two by a raise in temperature of 40 to 60° F., at an additional cost for heating of from 10 to 25 cents per ton of ore.

ACCESSORY TREATMENT.

Amalgamation.

The two extremes in the plate area provided for amalgamation prior to cyanidation are represented by the Rand and the Homestake. Figures from thirteen Rand plants, for the year 1913, show the recovery by amalgamation on mill feed, approximating $6.00, to be 61.4%, the plate area ranging from 0.25 to 2.0 sq. ft. per ton milled per day, and the mercury consumption about 0.1 oz. per ton milled. The tendency on the Rand has been to eliminate amalgamation directly after the stamps in favor of amalgamation after tubemilling, and at the same time, reduce the plate area to less than a half. In no case has the reduced plate area caused serious decrease in recovery by amalgamation, some instances showing no decrease, while, naturally, there is a decided saving in mercury loss, attendance and capital cost. On the other hand, amalgamation at Homestake is carried on both inside and outside of the stamp mortars and after regrinding. Of the total plate area of approximately 11 sq. ft. per ton milled, only 1.6% is used after regrinding. In 1914, on $4.11 mill feed, the Homestake recovery by amalgamation at the stamps was 69.0%, and after regrinding, 0.8%; the total of 69.8% being effected with a loss of mercury of 0.13 ounces per ton milled, at a total cost of 2.45 cents per ton milled.

Amalgamation, as practiced at the average plant, costs between 5 and 10 cents per ton milled, the plate area approximating 2 sq. ft. per ton milled. The recent trend has been to relegate to this step the recovery of such coarse gold as may greatly retard, or entirely escape, subsequent cyanide treatment. With amalgamation, crushing is nearly always done in water, although a few plants have been able to maintain their plates in fair condition when crushing in cyanide solution. The extremely low cost of recovering gold by amalgamation de-

mands that this step be given weighty consideration. An unusual method of amalgamation at the Nipissing H. G. mill is to be noted. A charge of 3 tons of 2500-oz. silver ore (containing 39% arsenic, 9% cobalt, 6% nickel), 4 tons of mercury and 1.5 tons of 5% KCN solution is tubemilled, with compressed air fed into the tube, for some 10 hours, at the end of which period amalgamation has recovered some 97% of the silver, the residues freed from amalgam and mercury then going to the cyanide plant. The mercury consumption is 20 lbs. per ton of ore.

Concentration.

Three general methods of concentration are practiced: (a) removal of high grade concentrates for shipment to smelters; (b) removal of lower grade concentrates for local treatment by cyanidation, or amalgamation or roasting followed by cyanidation; (c) removal of concentrates for finer grinding and returning to the regular plant pulp. A very complete concentration system, on a complex ore, is carried out by the Goldfield Consolidated, where approximately 6% by weight and 67% by value of the feed is removed at a cost for concentration of 6 cents per ton of ore concentrated, the concentrates then receiving a very successful local treatment. On the 26-oz. silver ore of the San Rafael (Pachuca), 1½% by weight and 22% by value is taken out as concentrate, to be shipped to smelter. On the high grade Esperanza (El Oro) sulphide ores, concentration removed 1.2% by weight, with 35% of the Au. and 16% of the Ag. Tonopah concentration removes approximately 15% of the Ag.; Stratton's Independence removes approximately 44% of the Au.; Liberty Bell, 8% Au. and 20% Ag.

The cost of concentration, per ton of ore concentrated. ranges from 5 to 15 cents—averaging perhaps 10 cents per ton. The apparent saving in the removal of refractory values and cyanicides by concentration, as reflected by decreased cyanide consumption and solution contact and lower assay value of final plant residue, must be carefully balanced against the higher cost of realization and loss in shipment of concentrates.

Local treatment of concentrates has engaged considerable attention and the following plants are cited:

Cyanidation of Concentrates.

Plant	Daily Production in tons	Assay ozs. per ton		% Extraction		KCN Cons. p. t. Concentrates	Cost per ton of Concts.						
		Au.	Ag.	Au.	Ag.	lbs.	Grinding	Roasting	Dissolution	Acid Treatment	Filtering	Precip. and Refining	Total
A—Goldfield Cons., Nev.	55	6.58		98.53		7.	.33	.82	2.34	.77	.30	.18	$5.68
B—Alaska Treadwell	75	2.92		96.5		2.3	.57		.78		.22	.81	2.81
C—Esperanza Mexico	1	22.68	54.2	99.4	95.8	6.0							4.85
D—Waihi, N. Z.	17	5.6	63.3	96.3	93.5	20.0							6.25
E—Geldenhuis Deep, Transvaal		16.0		98.75		3.3	3.65		2.67				6.32
F—Oriental Cons., Korea		2.2		93									2.87

Treatment.

A. Raw concentrates agitated in 2 lbs. KCN solution for five 8-hour periods, decanting after each period; after filterpressing, concentrates roasted in 2 Edwards duplex 54-spindle furnaces. Roasted concentrates agitated 8 hours in H_2SO_4 solution (20 lbs. acid per ton of concentrates). After four water washes, charge is neutralized and agitated in 2 lbs. KCN for five 8-hour periods, decanting after each. Then charge is tubemilled for 16 hours and sent to regular plant filter; 3 lbs. lead acetate per ton of concentrates. (J. W. Hutchinson, Min. and Scientific Press, January 25; February 1, 1913.)

B. Clean and docile pyritic concentrate, ground through 200 mesh; agitated in 1.5 lbs. KCN for 8 hours; decanted; agitated for 4 hours with barren solution; filterpressed and precipitated by zinc dust. (1911 Mine Report, Min. and Scientific Press, June 29, 1912.)

C. Tubemilled in 1.0 lb. KCN solution; agitated in 6 lbs. KCN for 10 to 14 days, with two decantations; filterpressed and precipitated by zinc dust; 2 lbs. lead acetate and 1 lb. mercuric chloride per ton of concentrates.

D. Tubemilled and agitated in 3 lbs. KCN solution for 8 to 10 days. (E. G. Banks, Min. and Scientific Press, January 21, 1911.)

E. Mill scrap and black sands. After amalgamation, the concentrate pulp for cyanidation (98%—200 mesh) assays 16.0 oz. Au. (R. Lindsay, J. C. M. & M. So., S. A.)

F. All sliming in tubemill with KCN, then 48 hours' combined air agitation and leaching, followed by filterpressing. (A. E. Drucker, Min. and Scientific Press, March 19, 1910.)

Aeration.

Oxygen absorbing compounds, such as pyrrhotite, hornblende, etc., not only cause an increased cyanide consumption, but frequently reduce the extraction of the gold by robbing the solution of its oxygen. Suitable oxidation of the pulp, prior to the application of cyanide solution, by forcing compressed air through the charge, renders many of these oxide consuming compounds harmless.

Roasting.

In the treatment of ore in which the gold is intimately associated, either physically or chemically, with such telluride compounds as sylvanite or calaverite, or with arsenical or antimony compounds, preliminary roasting is frequently the only known recourse. The practical object of the roast is to so liberate the gold as to permit ample contact with the cyanide solution and destroy deoxidizers and cyanicides. (A "dead" or "sweet" roast is usually essential.) The most extensive application of roasting is at Kalgoorlie, though some Cripple Creek ores receive this preliminary treatment, as do the graphitic ores of the Ashanti Goldfields. In the treatment of rebellious concentrates by cyanide, roasting plays an important part at the Goldfield, Nevada, plant. The usual furnaces are the Edwards, Merton, Pearce and Holthoff.

On the telluride ores of Kalgoorlie, crushed through approximately 28 mesh (0.0232″ aperture), roasting with Edwards and Merton furnaces costs approximately 65 cents per ton of ore. The sulphur content of the raw ores varies from 3 to 6%, although the elimination of the sulphur affords only a rough indication of the success of the roast. The hearth area, per ton of ore roasted per day, varies from 17 to 29 sq. ft. Consumption of wood varies from 10 to 13% of the weight of the ore. The temperature is approximately 650° F. Roasting

of Cripple Creek telluride ores at the Portland mill is done in one Holthoff and three Pearce furnaces, the daily tonnage being approximately 375. Costs per ton of ore roasted are as follows: Labor, operation, 11.02 cents per ton; labor, repair, 2.70 cents; coal, 31.55 cents; steam, 8.33 cents; power, 2.65 cents; miscellaneous supplies, oils, belting, water, lights, etc., 6.60 cents; total, 62.85 cents per ton.

Roasting of concentrates at the Goldfield Consolidated is done in two 54-spindle duplex Edwards furnaces, each having 1456 sq. ft. hearth area. The capacity of each furnace is given by J. W. Hutchinson as 40 tons of concentrates per day, although the amount roasted in the two furnaces is approximately 55 tons per day. The raw concentrates, after a preliminary cyanide treatment, assay 1.23 oz. Au. and 18.76% S, the sulphur, after roasting, being reduced to 0.90%. The cost of roasting, per ton of concentrate, is $0.82; while the complete cost of the two furnaces, dust flues, stack, 65'x158' steel building and miscellaneous bins and machinery amounted to $70,459.16. The concentrate loses 17% of its weight in roasting; and of the 1½% of the material passing out of the furnace as dust, only ½% is lost out of the stack. Five Merton furnaces for the roasting of 120 tons per day of Kalgoorlie sulpho-telluride ore cost $38,900.00. (M. W. Von Bernewitz, Mining and Scientific Press, April 11, 1914.)

Among the recent developments, mention should be made of the Holt Dern furnace used for a chloridizing roast. (F. Sommer Schmidt, Mining and Scientific Press, August 29, 1914.) On a daily tonnage of 150 tons, the costs are given as follows: Labor, 5.4 cents; power, 4.5 cents; repair, 2.0 cents; coal dust, 4.6 cents; salt, 35.0 cents; total, 51.5 cents per ton roasted.

Bromo Cyanidation.

With the object of dispensing with the roasting of telluride ores, bromo cyanide has been applied at several Kalgoorlie plants and at the Stratton's Independence, Cripple Creek. After a few hours' agitation with KCN, mixed potassium bromide and bromate salts, KCN and H_2SO_4 are added to the charge and agitation continued 4 to 20 hours. The consumption of the mixed salt is approximately 0.5 lb. per ton of ore.

Wet Desulphurizing.

At the Nipissing low-grade 240 ton mill, a complex arsenic antimony silver ore, carrying 26.0 ozs. Ag., is crushed and tube-milled in a 0.25% NaOH solution, and the thickened pulp is sent to the desulphurizing department, where it is tubemilled with aluminum ingots and agitated for 24 hours in mechanical stirrers lined with aluminum sheets.

After the filtration of the caustic soda, the pulp is agitated in a 5 lb. KCN solution for 48 to 60 hours. The cost of desulphurizing amounts to 48.0 cents per ton. The consumption of aluminum ingots and plates amounts to 1¼ lbs. per ton of ore. (J. Johnston, A. I. M. E., Vol. XLVIII, 1914.)

MAIN TREATMENT.

In the order of their prevalence, the standard systems of dissolution by cyanide may be classified as "slime agitation", "sand leaching", and "filter slime treatment". No widely accepted definition of "sand" and "slime" is in force. Practically, "sand" is the portion of the pulp treated by percolation, while the balance is considered "slime", and is treated by agitation or by pressure filtration. With the important exceptions of the large low-grade mines, such as the Rand and Homestake, the earlier practice of comparatively coarse grinding and treating sand and slime separately has largely given way to the present practice of finer grinding and treating the entire pulp as a single product, on the smaller properties. "All sliming" is the term applied to the latter system. With separate sand and slime treatment, the slime is usually cone classified and averages about 90% thru 200 mesh (0.0029″). In all-sliming plants, the pulp varies from 60 to 90%, through 200 mesh, depending on the economical limit of fine grinding and subsequent treatment. In sand and slime plants, crushing is almost universally done in water, while with all-sliming, crushing in cyanide solution is almost universal.

SLIME AGITATION.

Thickening.

Pulp from the grinding plant is received at dilutions ranging from 3.0 to 14.0 to 1, a common figure being 6.0 to 1.

To reduce the initial cost, expense and difficulty with the agitation and subsequent equipment, the mill pulp is thickened to a dilution approximating 1.5; although under special conditions the dilution is as low as 0.5, with unusually quick settling granular slime, and as high as 3.0 with poor settling, flocculent or amorphous slime. This thickening is, in some cases, done with filters, cones, spitzkasten, or decanting tanks, although modern practice distinctly favors the Dorr continuous mechanical thickener.

Dorr Continuous Mechanical Thickener.

Naturally, there is no standard size recommended or used, as this depends on the capacity desired, settling qualities of the pulp, density to which thickening is to be carried, clearness of overflow, alkalinity, temperature, and dilution of the feed. As a general rule, it may be stated that approximately 6 sq. ft. of tank area are needed per ton of granular slime per 24 hours, while 10 to 15 sq. ft. should be allowed for flocculent slime. The writer finds that several installations in different localities show an average of $2,500.00 for the complete erected cost of a standard, steel, 30′x12′ unit. In terms of tonnage of dry slime handled per 24 hours, the capacity of a 30′x12′ standard thickener, under normal conditions, may be given as 125 tons of granular slime and 65 tons of flocculent slime, making the erected cost of the thickener $20.00 and $38.46, respectively, per ton of daily capacity.

While the present trend is toward shallow tanks, of 5′ or 6′ depth, as shown in the use of the submerged type of tray thickener, the former practice of deep tanks is of no mean value, in that it affords considerable storage space. However, the tray thickener offers a quick and cheap means of increasing the capacity of an existing installation of standard thickeners. In a general way, the addition of a tray may quite safely be expected to show a 75% increase in capacity over a standard thickener. The power requirement of a 30′x12′ standard unit run at 1/5 r.p.m. is about ¼ hp., the cost of operation approximating 1 cent per ton of ore.

Agitation.

The matter of proper dilution at which pulp should be agitated is one demanding careful consideration for each in-

dividual plant. Experimental work points to high dilutions, but practical considerations generally necessitate as thick a pulp as can be regularly drawn from the thickeners. A dilution of 1.5 is, perhaps, an average. Inasmuch as the cost of agitating a ton of slime for 24 hours should not exceed 3 cents, it is evident that the agitation period, to be commensurate with this low cost, should be well advanced toward the point where further dissolution ceases. In determining the proper length of agitation, such items as capital charge on the agitators and accessories, consumption of cyanide, lime and other chemicals, possible premature precipitation of dissolved metals in prolonged agitation, and the mechanical cost of agitating, should be carefully balanced against the net returns from the metals dissolved. Then, too, the possibility of decreasing the fineness of grinding by prolonging the agitation should be examined.

The modern trend is in favor of continuous agitation, as compared with the former intermittent system. Change of solution during agitation is found advisable with certain ores; although with present day agitators, capable of giving ample aeration, the entire agitation step is frequently carried out in one stage.

The four types of agitators in present day use may be classified as: (1) mechanical, (2) pneumatic, (3) combined mechanical and pneumatic, (4) pump transfer. Limited space allows mention of only those most commonly used.

The pump transfer system is in extensive use on the quick settling and readily soluble Rand slime, for which some four hours of circulation or agitation suffice. This system of agitation is seldom found elsewhere and will not be included in the following comparison, which is based on practically identical working conditions.

Mechanical Agitator.

Top-drive paddle-arm stirrers or agitators were used from the start of the slime agitation process, and, with proper design, still hold a fair place at this day. The bottom-drive agitator, as used in Kalgoorlie, Mexico, and the Rand, eliminates the submerged step bearing of the top drive, allows of a simpler overhead construction, and due to the increased rigidity of the

drive, operates with very moderate power. Assuming a tank 30 ft. diameter by 12 ft. deep as an approximate standard, a satisfactory agitating speed for the bottom drive type may be given as 8 r.p.m. and the power as 6 hp. In addition, the power for furnishing 20 cu. ft. of free air per minute at 10 lbs. pressure, for requisite aeration, amounts to 1 hp., making the total power requirement 7 hp. This type of agitator works quite satisfactorily, although it is troublesome to start up after a protracted shut-down, tends to bank up near the center and gives *en masse* agitation. Inclined baffle boards bolted to the side of the tank will materially assist agitation. An average erected cost of a 30′x12′ bottom-drive, steel-tank, mechanical agitator may be given as $2,395.00. Such a tank will have an available depth of 11 ft. 6 in., and, with pulp at a dilution of 1.5, will hold 134 tons of dry slime, making the total erected cost $17.87 per ton of dry slime capacity.

Pachuca (or Brown) Agitator.

This pneumatic agitator is, perhaps, the most widely used in present day practice. Although numerous variations have been made in the size and equipment of these tanks, the standard is 15 ft. diameter by 45 ft. total height, a 60° cone forming the bottom. The central air-lift is 15″ or 18″ diameter and extends to within a few inches of the top of the tank. The special sleeve valves are quite often dispensed with. A spare air hose, used at regular intervals, assists in preventing accumulations on the sides of the cone and tank. The air consumption is varied to suit the desired intensity of agitation and the character of pulp. Figures from installations of the standard size show an air consumption ranging from 50 cu. ft. of free air per minute, on flocculent slime, to 125 cu. ft. on quick settling granular slime, at pressures ranging from 25 lbs. to 40 lbs. Average figures indicate a consumption of 70 cu. ft. of free air per minute at 30 lbs. pressure, requiring approximately 7.0 hp. The total erected cost of a 15 ft. x 45 ft. steel Pachuca agitator will average $1,935.00. With an available depth of 44 ft. and with pulp at a dilution of 1.5, this tank will hold 102 tons of dry slime, making the total erected cost $18.97 per ton of dry-slime capacity.

Dorr Agitator.

This comparatively new type of agitator, combining mechanical and pneumatic agitation, has met with merited success. It is usually operated at 3 r.p.m., the speed depending, of course, on the character of the pulp. Under average conditions, a 30 ft. x 12 ft. Dorr agitator will require about 1.5 hp. for moving the arms, at 3 r.p.m., and 2.5 hp. for furnishing 30 cu. ft. of free air per minute at 20 lbs. pressure, a total of 4 hp. The total erected cost of such an agitator with steel tank will approximate $2,510.00. With an available depth of 11 ft. 6 in. and with pulp at a dilution of 1.5, this agitator will hold 134 tons of dry slime, making the total erected cost $18.73 per ton of dry slime capacity.

Capital Costs of Slime Plants.

It may be of value to cite approximate figures from Rand practice, where the intermittent decantation and pump transfer type of plant has reached such high development. Data given in "Rand Metallurgical Practice", Vol. II, show the total approximate capital costs of slime plants, in dollars per ton of slime treated per 24 hours as follows: 150 to 225 tons, $292.00; 300 to 450 tons, $276.00; 600 to 900 tons, $260.00; 1200 to 1800 tons, $243.00. Such slime plants provide for collecting and two washes, two days being available for collecting and treatment, and include complete pulp, solution, decanting and water services, together with solution clarifiers, but exclude precipitation, refining and power plants. It must be noted that Rand plants require very little expenditure for buildings.

Cost of Dissolution by Slime Agitation.

Costs of dissolution may be of some interest, although it must be remembered that such costs depend on numerous widely varying conditions, such as character and grade of ore, cost of labor, power and supplies, amount of extraction effected prior to agitation, arrangement and capacity of the plant, and the recovery percentage achieved. Furthermore, such accessory steps in the cyanide process as fine grinding, filtration or decantation, precipitation, melting and refining, will depend on the dissolution method in use and, hence, should be taken into account in comparing "slime agitation" with "sand leaching" or "filter treatment". Then, too, the higher percentage

Comparative Agitator Data.

M.—Bottom Drive Mechanical
P.—Pachuca
D.—Dorr

Sp. Grav. of Pulp = 1.326 (L:S = 1.5:1)
Power at $5.00 per hp. per month.
Labor at $3.00 per 8 hr. shift.

Type	Size	Capacity. Dry tons of slime	Total erected cost	Erected cost per ton of capacity	Power per 100 tons of slime	Total operating and repair cost per ton of slime per 24 hrs.—500 ton plant
M	30′ x 12′	134	$2395.00	$17.87	D—3.0 hp.	D—1.8 cents
D	30′ x 12′	134	2510.00	18.73	M—5.2 hp.	P—2.3 cents
P	15′ x 45′	102	1935.00	18.97	P—6.9 hp.	M—2.4 cents

Agitator Requisites	Violence of agitation	Total operating cost per ton	Regulation of amount of air for aeration	Freedom from choking or settling	Ease of starting after shut-down	Adaptability to			Operating Simplicity	Minimum loss in mill height
						Varying pulp conditions	Continuous system of agitation	Selective agitation		
In	P	D	M	D	P	P	D	D	P	D
order of	D	P	D	P	D	D	P	P	D	M
preference	M	M	P	M	M	M	M	M	M	P

of dissolution obtained by "slime agitation" must be weighed against the value of the dissolved metals and cyanide lost by imperfect filtration or decantation. It is to be understood that the following figures are merely numerical averages of compilations from representative plants in various parts of the world. The cost of dissolution per ton of slime is made up of the charges for thickening, agitating, proportionate pumping, supervision, cyanide, lime and lead salts.

	Cost of dissolution	Cost of filtration or decantation precip. and refining	Total
Average gold ore.....	$0.29	$0.25	$0.54
Average silver ore.....	0.83	0.42	1.25

Included in the above, but so far below the average as to require special notice, is the intermittent decantation method practiced on the Rand, where the slime is particularly amenable, in so far as concerns thickening, dissolution and chemical consumption. Figures from nine Rand slime plants show an average cost for dissolution, decantation, precipitation and refining, of 24.5 cents per ton of slime, the extraction averaging 85.9% on slime heads of $1.92. Recent Rand slime plants have adopted filtration in place of decantation, and obtain extractions ranging from 92 to 95%. From the above Rand figures, about 4 cents should be deducted for precipitation, refining and assaying.

SAND LEACHING.

The Rand is the greatest present day exponent of sand leaching, comparatively few plants in other parts of the world retaining separate sand and slime treatment. The important improvements made in fine grinding and the handling of slime created a marked tendency toward all-sliming and the abandonment of sand leaching, this trend, in a few instances, resulting in inadequate consideration of the question of highest commercial recovery versus highest theoretical extraction. A few all-sliming plants, after careful research and consideration, have found it advisable to revert to the former sand and slime

practice. But even in the strongholds of sand leaching, the present day trend is toward finer grinding and a gradual reduction in the proportion of total mill pulp treated by percolation.

Careful classification or separation of sand and slime is highly imperative and cone classifiers of the hydraulic and diaphragm types are almost universally used. Collector tanks have been abandoned, in a number of recent Rand plants, in favor of continuous collection by sand filter tables, the cost of operating these sand filters approximating 3 cents per ton of sand. The use of sand filter tables is reported to represent a saving in capital cost of plant (as compared with the usual intermittent type of plant) of some 13 to 25%, depending on the size of the plant, and, in addition, the filter-collected sand is cleaner and drier.

The collecting tanks, now made of steel, are usually charged by revolving distributors. The discharge of the sand residue from treatment tanks, which now range up to 70 ft. diameter by 12 ft. deep, is accomplished by sluicing, shovelling, or mechanical excavators, the method depending on local factors such as cost and abundance of water, and labor and storage requirements. A recent trend in the method of sand-residue disposal has been to sluice the sand into dewaterers, or classifiers, from which it gravitates underground, for stope filling. The destruction of the cyanide present in the residues is accomplished, where necessary, by the addition of some 0.08 lb. of $KMnO_4$ per ton of sand. Since its introduction on the Rand, sand filling of stopes has been very advantageously adopted in other countries.

Rand Metallurgical Practice, Vol. II, p. 418, gives the following comparison of the cost per ton for transferring drained sand from tank to tank: (a) by truck haulage, 3.96 cents; (b) by shovelling and conveyor belt, 3.36 cents; (c) by shuttle belts and main conveyor belts, 2.44 cents.

Capital Costs of Sand Leaching Plants.

Data in Rand Metallurgical Practice, Vol. II, pp. 347-350, give estimates of unusual value. The sand plants are of the standard type, allowing four days for collecting and eight days for treatment. The costs include classifying cones (yielding

70% sand), collecting and treatment tanks, revolving-pulp distributors for collecting tanks, belt-conveyor transfer system to treatment tanks, water and solution services, and sand-residue disposal plants, but exclude precipitating, refining, and power plants. The capital expenditures for various capacities of above plants, per ton of sand treated per 24 hours, are as follows: 350 tons of sand per day, $264.00; 700 tons, $254.00; 1400 tons, $244.00; 2800 tons, $233.00.

Estimated capital costs of sand plants using continuous sand-filter collecting, yielding 55% sand, are given as follows: 275 tons of sand per day, $230.00 per ton of daily sand capacity; 550 tons of sand, $212.00; 1100 tons of sand, $195.00; 2200 tons of sand, $177.00.

The actual combined cost of the two Homestake sand plants, of a total capacity of 2500 tons, amounted to $255.00 per ton of daily sand capacity. This figure includes power, heating, precipitating, and clean-up plants.

Operating Costs of Sand Leaching Plants.

In offering sand-leaching cost data, it may be well to cite the working of a few representative plants. Again, it must be noted that no comparisons are here intended, local conditions being at too great a variance.

Rand.—Fifteen Rand plants show that an average of 57.6% of the mill pulp is leached as sand by double treatment, the proportion ranging from 70% sand in the older plants, to 40% sand in recent plants. The economical limit of fine grinding of the sand approximates 70% through 100 mesh (0.0058″ aperture). With intermittent collecting, revolving distributors are preferred to hose filling. The transfer of the drained sand to the treatment tanks is by truck haulage, or by shovelling, in cases where the collectors are superimposed upon the treatment tanks. With continuous sand-filter collecting, the collected sand is transferred by conveyors or pumped to revolving distributors. The residue is discharged by belts, trucks, buckets or sluicing into cone dewaterers for sand filling of stopes. The total ratio of solution to sand for dissolving and washing approximates 1.5 to 1. About four days are allowed for collecting and draining and seven to eight days for treatment. Approximately one ton of solution is precipitated per

ton of sand. The strong solution is about 2 lbs. KCN, while the weak is about 0.5 lb. KCN.

Figures from ten Rand plants for 1912, with daily sand tonnage running as high as 3500 tons, show the following averages:

Total cost of sand treatment per ton of sand (including classification, collecting, treating, precipitating, refining and residue disposal), ranging from 37 to 45 cents, average	39.8 cents.
Average extraction on $3.17 sand heads	79.8%
Average extraction in recent sand plants	89.5%

Homestake.—Average 1914 daily tonnage, 2500 tons of sand, or 55% of the mill pulp. Two single-treatment sand plants, consisting of twenty 44′x9′, 600-ton, and five 54′x13′, 1250-ton treatment tanks. Single treatment, or collecting and treatment in same tank; 9 hours required for collecting by revolving distributors. Two treatments with 2.5-lb. KCN strong solution and one treatment with 1.3-lb. KCN weak solution are each preceded by draining and aerating, with air at 4 to 5 lbs. pressure. The final water wash is followed by sluicing—one ton of sluicing water being required per ton of sand.

Total solution used per ton of sand	0.8 tons.
Total solution precipitated per ton of sand	0.4 "

Total cycle approximates seven days. Screen sizing of sand: + 100 mesh, 28.5%; — 100 + 200, 35.1%; — 200, 36.3%.

Consumption per ton of sand; sodium cyanide, 0.232 lbs.; zinc dust, 0.062 lbs.; lime, 3.11 lbs.; power, 0.972 kw. hrs.

Extraction on $1.42 sand heads	78.7%
Total cost of sand treatment per ton of sand	17.8 cents.

Pittsburg Silver Peak.—Average 1911 daily tonnage, 320 tons of sand, or 60% of the mill pulp. Single treatment in five 36′x11½′, 480-ton tanks; 50 hours of 3-lb. strong cyanide solution leaching is followed by draining and aeration, and then 25 hours of 1.5-lb. weak solution is followed by the final wash.

Collecting is by revolving distributors, while the residues are sluiced out with one ton of water per ton of sand.

Total cycle approximates seven days. Screen sizing of sand: + 35 mesh (0.0164″), 23%; — 35 + 65 (0.0082″), 29%; — 65 + 100, 21%; — 100 + 200, 18%; — 200, 9%.

Extraction on $3.15 sand heads..... 79.9%

(It is to be noted that a tubemill was recently installed to increase the fineness of the above stamp battery product.)

Cost of sand treatment per ton of sand, exclusive of neutralizing, precipitating, refining and assaying, 23.5 cents.

Itemized statements of the cost of sand leaching may prove of value. The Rand data, taken from R. M. P., Vol. I, p. 186, are based on 27,716 tons of sand (per month?) representing 56.4% of the total mill pulp, continuous sand-filter collecting being in use.

Cost of Sand Treatment per Ton of Sand.

Rand.		Homestake.	
Labor	6.54 cents	Superintendence	1.06 cents
Assaying, sampling	0.32	Assaying	.48
Lime	0.56	Neutralization	1.54
Transferring, discharging	8.62	Transportation	.17
Cyanide	7.23	Classification	1.18
Precipitation	1.56	Treatment	8.59
Zinc shavings	1.28	Precipitating and pumping solutions	1.18
Clean-up, smelting	2.92	Refining	.38
Sodium bisulphate	0.94	Heating	.51
Miscellaneous supplies	2.30	Miscellaneous	.81
Water	1.60	Repairs	1.88
Power and lights	6.48		
Miscellaneous	0.59		
Total	40.94 cents	Total	17.78 cents

FILTER SLIME TREATMENT.

Direct filter treatment has so far been limited to a comparatively few plants in Kalgoorlie, and to the Homestake and Silver Peak, in America. However, where the slime is of such

a nature that a solution contact of some four to eight hours is ample, direct filter slime treatment is, perhaps, the most efficient and satisfactory practice of the day. The partially thickened slime, in water, is charged directly into the filters, where the slime cake is in an excellent condition to receive preliminary treatment, such as aeration, solution leaching, and washing. The entire dissolution is effected in the filter, with a minimum amount of solution, precipitation, consumption of chemicals, power and labor, and loss in dissolved gold. The plant is very simple and compact, while the various operations are susceptible of accurate technical control.

Two examples of direct filter treatment are cited to indicate the results being obtained.

Pittsburg Silver Peak.—Daily capacity, 200 tons of slime. Treatment is effected in three 86-frame Merrill automatic-sluicing pressure filters, the total cycle requiring four hours. The extraction on $1.55 slime heads is 92.2%. The total cost of treatment, including dissolution, filtration and discharging, is as follows:

Labor at $4.50 per 8 hrs.	7.3 cents
Repairs	1.2
Power for pumping, filtering and air at $7.37 per hp. month	3.6
Cyanide (98% at 21.47c per lb.)	11.4
HCl at $6.87 per carboy	0.5
Canvas	1.1
Miscellaneous supplies	1.2
Total cost per ton of slime	26.3 cents

Homestake.—Daily capacity, 1925 tons of slime. Treatment is effected in twenty-eight 90-frame Merrill automatic-sluicing pressure filters, the total cycle requiring nine hours. The extraction on $0.92 slime heads is 89.9%. The ratio of total solution used per tone of slime is 1:1, of which only 0.7:1 is precipitated. Loss in dissolved gold per ton of slime is ¾ cents.

Total Cost of Homestake Direct-Filter Slime Treatment per Ton of Slime.

Superintendence	0.93 cents	Or, combined as:—	
Assaying	.31	Works labor	6.70 cents
Neutralization	2.03	Shop labor	.84
Thickening	.34	Power	1.84
Treatment	10.73	Chemicals	6.78
Precipitating and pumping solutions	1.65	Miscellaneous	2.22
Refining	.66	Total	18.38 cents
Heating	.17		
Miscellaneous	.88	**Consumption per ton of Slime.**	
Repairs	.68	Sodium cyanide	0.161 lbs.
Total	18.38 cents	Zinc dust	0.118 "
		Lime	3.840 "
		HCl	0.393 "
		Power	1.150 kw. hrs.

Actual cost of dissolution, deducting precipitation, refining, assaying, and 1/3 of superintendence and miscellaneous items ..... 15.16 cents

Capital Cost of Direct-Filter Slime Treatment Plants.

Assuming an average total cycle of six hours, the complete capital cost, including classification, thickening, filters, precipitation, refining, pumping, heating—all enclosed in buildings—will approximate $265.00 per ton of daily slime capacity.

DISCUSSION

Mr. Clennell.

Mr. J. E. Clennell called attention to a recent experience in the cyanidation of a silver ore, where an oxidizing roast rendered the silver refractory. He asked if any of the metallurgists present had had a similar experience.

Mr. Merrill.

Mr. C. W. Merrill,* Mem. Am. Inst. M. E., stated that he had had a similar experience.

Prof. Clevenger.

Prof. G. H. Clevenger,† Mem. Am. Inst. M. E., said that the peculiar behavior of silver ores when subjected to an oxidizing roast had come to his attention some ten or twelve years ago, but that he did not realize the full significance of it until later. If you wish to ruin the extraction of any silver ore, give it an oxidizing roast. He further stated that closely related to the behavior of silver ores during the oxidizing roast is the effect of oxidation which at times takes place with silver ores in nature. It has been his experience that, on the whole, surface silver ores

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were more difficult to treat than ores coming from the lower levels, and this is just the reverse of what is generally true of gold ores. He also called attention to the behavior of the so-called manganese silver ores and expressed the thought that the refractory nature of these ores was not due so much to combination of the silver with manganese, as to the influence of the manganese mineral as an oxidizing agent upon the silver in whatever form it may have been originally deposited in the ore. Prof. Clevenger.

Mr. Chas. Butters,* Mem. Am. Inst. M. E., called attention in this connection to the difficulty in treating flotation concentrate. He said that a satisfactory extraction could not be made upon the concentrate as produced and from a silver ore; and should it be roasted, it would still be impossible to recover the silver. Mr. Butters.

Mr. C. T. DuRell,† Mem. Am. Inst. M. E., did not think that the comparisons given in the paper of roasting practice in Cripple Creek and Australia were quite fair. He called attention to the fact that the furnaces which had been developed and built locally had given better satisfaction than the American furnaces, and that it was not true that the Edwards furnace was displacing the Merton furnace. He further said that he did not agree with Mr. Butters' statement that flotation concentrate could not be cyanided. He did, however, agree with the statement that, when concentrate containing silver is roasted, it cannot be cyanided. He further reasoned that the refractory nature of the raw concentrate was due to something that had been added during flotation; therefore, he thought that the difficulty must be due to either oil or air. Through a process of elimination, he was led to the belief that the difficulty was due to the oil; however, he thought that through heating or treating the concentrate with a special solvent for the removal of the oil, the difficulty could be overcome. Mr. DuRell.

Prof. Clevenger said that he did not think that he had sufficiently proven his point, since it is a well-known fact that certain oils do combine with certain metals and that it is not improbable that oils might combine with certain of the minerals present to form a chemical combination. Prof. Clevenger.

Mr. DuRell asked what the nature of the compounds formed would be. Mr. DuRell.

Prof. Clevenger replied that he was not prepared to go into the chemistry of the matter at the present time, on account of lack of proper investigation of the subject. Prof. Clevenger.

Mr. Merrill thought that the difficulty might be due to a physical cause and that, therefore, the cause of the difficulty could not be limited, as Mr. DuRell had attempted, to air and oil. Mr. Merrill.

Mr. Butters stated in conclusion that he had gone into the matter sufficiently fully so that he was absolutely sure that the treatment of flotation concentrate presented serious difficulty. Mr. Butters.

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Paper No. 187

FILTRATION OR SEPARATION OF METAL BEARING SOLUTION FROM SLIME RESIDUE.

By

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Probably the most vital point in the practical application of the cyanide process is the filtration or separation, after dissolution, of the metal bearing solution from the slime residue. Certainly no other point has called forth such a combination of inventive ingenuity and practical ability as has been expended in developing a satisfactory technical and economical solution of this problem.

The reason for this is readily appreciated when one stops to consider that for every unit of dissolved metal finally discharged with the residue, there is incurred a net loss equal to the market value of the unit plus the mechanical loss of cyanide, amounting to a further $.05 to $.10 per ton. Since filtration or decantation is almost the last step in gold and silver production, and amounts at most to 5% of the total cost, there is obviously every incentive to obtain the highest possible efficiency.

Many attempts have been made to arrive at a scientific designation of so-called "slime". None of them, however, has been entirely satisfactory, and, for the purposes of this article, the writer has in mind the practical definition of most mill men, namely, "that portion of the ore which, after crushing and grinding, will not leach economically in open vats at atmospheric pressure".

The amount and character of this material produced will depend chiefly upon the nature of the ore and upon the degree

of comminution necessary to obtain an economic extraction. Many so-called "all-slime" plants find it feasible to agitate and filter, or decant, a product of which fully 40% will remain upon a 200 mesh screen, while others grind to a point where only a fraction of one percent will remain upon this mesh. The governing factors are purely individual, such as size and nature of plant, location, character of ore, etc., and can hardly be generalized.

In the earlier days of the cyanide process, the slime portion of the ore was by far the most difficult to treat, and in crushing, every precaution was taken to insure a maximum of granular product. With the development of the decantation processes, however, and of slime filters, which came later, the position was completely reversed, and slime treatment may now be carried out at least as economically as sand treatment. A natural tendency toward "all-slime" treatment has thus developed, and for plants of less than 200-tons daily capacity has become, at the present time, almost universal. Processes involving sand leaching are now considered applicable only to large plants, and, in particular, to those treating low-grade material.

All ores after fine grinding may be classified into two products—granular and amorphous, and most of the difficulties experienced in slime filtration and decantation may be traced to extreme conditions as regards either the one or the other.

An undue amount of coarse, granular material will not only increase the power consumption in the agitators and thickeners, but will also choke and cause frequent interruptions, and unless filtered at 50% moisture, or less, will result in classification and uneven washing.

On the other hand, where the percentage of amorphous is high, it is seldom possible to thicken to less than 60% moisture, even with a very large settling area, and a pulp of this dilution will not give economic results with either continuous or intermittent decantation, and even for filter treatment requires a largely increased area and frequently results in slow and imperfect washing. Cracks and channels will also develop with any type of filter in which the cake is exposed to the air before or during washing.

It may be safely stated that for ideal slime-washing results with any of the methods now in vogue, an all-slime product should fulfill the following conditions:

It should be ground in a closed circuit with suitable classifiers, so that not more than 25% of the total product will remain upon a 200 mesh screen and all of the metallic or sulphide portion will pass the same aperture.

It should settle from 85% moisture to at least 50%, with a continuous settling area of from 6 to 10 sq. ft. per ton of dry solids per day.

The various processes and machines now in general use for thickening, decanting and filtering slime are here enumerated. The list is by no means complete, but includes equipment which probably handles over 95% of the slime tonnage produced in the cyanide process throughout the world. Very complete descriptions of these machines have appeared from time to time in the technical press and will not be here repeated, the object of this paper being rather to bring out the salient points in the operation of each machine and such recent cost data as may be available.

Thickening:
- Dorr Continuous Thickener
- Settling Tanks

Vacuum Filtration:
- Butters Leaf
- Moore Leaf
- Oliver Drum
- Portland Drum
- Ridgway Leaf

Pressure Filtration:
- Merrill Sluicing Plate-and-Frame Press
- Dehne Type Plate-and-Frame Press
- Kelly Enclosed Leaf
- Burt Revolving Cylinder

Continuous Decantation:
- Dorr System

Intermittent Decantation:
- Rand System

THICKENING.

As a preliminary adjunct to any filter operations, the pulp is first settled to a minimum moisture content; in average practice this will be found to approximate closely to 50%, or equal parts of liquid and solid. In some plants this thickening is all done prior to dissolution, while in others, thickeners are used both before and after the agitation.

For filtration, the moisture should be reduced to such a point that the heavier particles will remain in suspension, or at least settle very slowly during the cake-forming period. This governs the uniformity of the cake and is one of the most vital points in all filter operations, and since the size of the largest particles is, in turn, governed by the limits of economic grinding, the required buoyancy is best obtained by proper thickening.

The use of the Dorr continuous thickener has become almost universal for this work in America, and is being largely adopted in foreign countries as well. The machine requires a minimum of power and attendance, and when used in conjunction with a diaphragm pump or air lift for elevation, the discharge may be operated with practically no loss of mill head. Discharges as low as 33% moisture are obtained in the Porcupine District, but on other ores, careful attention may be needed to obtain 60%.

On the Rand, with colored labor at $0.75 or less per day, and power at $5.50 per hp.-month, it is still found economical to retain the large intermittent settlers. These are steel tanks, varying from 50 ft. to 70 ft. in diameter, with from 10-ft. to 14-ft. sides and cone bottoms, giving an additional depth of from 4 to 8 feet. Peripheral overflows and adjustable decanting arms are provided, and the tanks are emptied by sluicing the settled slime into the suction of a centrifugal transfer pump.

This system of settling or dewatering is particularly well adapted to African conditions, where flat open mill sites are used, and where all tanks are unhoused. But it is to be noted that while the intermittent settlers on the Rand, particularly during the warm summer months, frequently settle down to 40%, and even to 38%, moisture, the best that continuous thickeners seem able to do is 50%. Since this extra 10% of

water must be brought up to treatment strength in cyanide, and then wasted, its elimination is obviously highly desirable. With any settling equipment, satisfactory moisture figures are seldom obtained during the winter months, when 60% is more nearly the average figure, with, of course, the attendant temporary high losses in cyanide and gold.

As illustrations of thickening equipment operated in special cases, there may be mentioned the vacuum leaf filters at Waihi, New Zealand, where a moisture of 30% is obtained prior to cyanide treatment, and the deep conical-bottom continuous settlers used for thickening to 66% moisture prior to direct cyanide treatment in Merrill slime filters at the Homestake.

The area required for proper continuous settling is, of course, mainly a function of the nature of the ore and dilution of the pulp, and varies from 4 to 15 square feet per dry ton of daily capacity, with a pulp feed of from 90 to 75% moisture.

With intermittent settling, as practiced on the Rand, the period required for discharging introduces an additional time factor, and it is usual to allow from 14 to 25 sq. ft. per ton of dry slime. It should be noted that, in this practice, practically all the water used in crushing and classification goes to the slime collectors, which thus handle a feed containing from 90 to 95% moisture.

The cost of thickening operations will vary from $0.005 to $0.02 per ton of ore milled, depending upon local conditions and the scale of operations.

VACUUM FILTRATION.

The Butters Filter.

Of the submerged leaf vacuum filters, the Butters is by far the most widely used. Developed first in the United States and Mexico, its use has now spread throughout the world.

As originally operated, the leaves were closely stitched and a reverse pressure of either air or water, or both, used to dislodge the cakes after washing. A recent development has been the elimination of all sewing in the body of the leaf, the discharge of cake being effected by equalizing the pressure on both sides of the filter surface. The net result is a longer canvas life and a much clearer filtrate. The control of the various

operations of the filter, from a central switch-board, has also very much simplified the handling of an otherwise somewhat complicated mechanism.

The Butters filter was first installed on the Rand, at the Crown Mines, in 1910, and has been adopted in all the new plants erected there since that time, as well as in some of the older remodeled plants. The slime produced from milling the banket ore is almost entirely free from amorphous material, and is, therefore, ideal for filtration. Very excellent washing results are obtained, with moderate operating costs. By means of spray pipes, the sides of the filter box, and also the transfer pipes and pumps, are flushed between each transfer, thus minimizing the former troublesome admixture of wash solutions and pulp.

Under conditions obtaining on the Rand, the average operating costs of the Butters filters may be stated as follows:

Labor	$0.0168
Power	0.0212
Supplies	0.0143
Air	0.0044
Repairs	0.0084
	$0.065 per ton filtered.

The caking effluent approximates $2.00 per ton, and the dissolved loss seldom exceeds $0.05. These figures are for plants filtering from 600 to 1000 tons of slime daily.

Two of the chief difficulties the African metallurgist has to contend with are poor settling and poor precipitation during the winter months. Together they may cause very sudden and very high losses in a decantation plant. Filtration, on the other hand, provides a positive wash and fixed moisture in the residue, and if necessary, permits the use of a short final water wash. This is the chief reason why filtration has been installed on many of the higher grade mines, and while the operation of slime plants equipped with Butters filters may be stated as approximately $0.06 higher than for those using decantation, the total recovery is also higher by $0.12, averaged throughout the year, leaving a net gain of $0.06 in favor of the filter.

As typical of one of the most successful Butters plants in America, may be cited the Goldfield Consolidated. This installation has a capacity of 850 tons per day with 336 leaves, or 50 pounds per sq. ft. of area per day. According to J. W. Hutchinson (Mining and Scientific Press, May and June, 1911), the value of the caking effluent is $4.00, and the dissolved loss $0.06. Operating costs are:

Labor	$0.036
Supplies	0.012
Power	0.022
	$0.07 per ton filtered.
	(Since reduced to $0.05).

At the plant of the Nipissing Mines Co., at Cobalt, an 80-leaf Butters filter handles 240 tons, or 66 pounds per sq. ft. of area per day. This is a silver ore, very granular, and ground extremely fine, making an ideal filter product. Operating costs are given by James Johnson (A. I. M. E., Jan., 1914), as:

Power	$0.034
Labor	0.072
Supplies	0.041
Miscellaneous	0.015
	$0.162 per ton filtered.

Other Butters operating costs are as follows:

McNamara, Tonopah	150 tons	silver	$0.237	per ton filtered
Montana-Tonopah, Tonopah	146 "	"	0.230	" " "
Loretto, Pachuca	700 "	"	0.07	" " "
Flores, Guanajuato	160 "	"	0.06	" " "
Dos Estrellas, El Oro	750 "	gold	0.075	" " "

The Moore Filter.

The Moore vacuum leaf filter differs from the Butters, in that the filter leaves are lifted at intervals and transferred successively to the pulp, wash solution and discharge compartments, instead of using a stationary leaf and effecting the various transfers with centrifugal pumps.

The Moore filter has been widely used in Mexico, particularly at Pachuca, and a number of plants are also in operation

in the United States, Canada and in Australia and New Zealand.

The Moore filter plant at the Victoria mill of the Waihi Gold Mining Company, as described by Wm. McDonald in the C. M. & M. Society for May, 1913, gives some remarkably efficient figures. For this 1000-ton filter, the operating costs are given as follows:

Power	$0.0288
Labor	0.0554
Supplies	0.0114
Miscellaneous	0.0040
	$0.0996 per ton filtered.

The caking effluent averages $4.60 gold and 1.72 oz. silver, while the dissolved loss is stated to be $0.048 in gold and 0.02 oz. in silver.

Other Moore filter costs are as follows:

Hollinger, Porcupine	600 tons	gold	$0.103	per ton filtered
Liberty Bell, Colorado	430 "	gold and silver	0.099	" " "
La Blanca, Pachuca	300 "	silver	0.105	" " "
San Rafael, Pachuca	400 "	silver	0.110	" " "

Note.—These costs do not include royalty.

The Ridgway Filter.

The Ridgway reciprocating vacuum leaf filter differs from the Moore, chiefly in that the leaves are suspended from arms which swing in a vertical plane, through an arc of approximately 180°, from pulp to wash tank, the final discharge taking place when the arms are vertical. This filter is reported as doing good work in Australia, but operating costs and data are not available at this time.

A difficulty common to this filter, and to all operating on the Moore principle, is that the originally barren wash-solution tank builds up in value due to diffusion of rich solution from the slime cakes. This may be remedied in part by clarifying and re-precipitating a sufficient volume to keep the wash at the desired figure, which should not exceed $0.05 for good work.

REVOLVING DRUM VACUUM FILTERS.

The Oliver Filter.

Of this type, the Oliver is one of the first and by far the most widely used. The fact that the machine is continuous in operation and reduces labor and supervision to a minimum has made it a most valuable adjunct to small plants handling from 30 to 150 tons per day. Owing to the nature of the cake, and the limited time available for washing, a complete displacement of dissolved values is difficult of attainment, but this often becomes of minor importance with low-grade ores, and richer solutions may be handled by giving one or more decantations ahead of the filter.

It is, in fact, in conjunction with continuous decantation that the Oliver probably finds its most useful field in cyanide metallurgy. It combines really continuous operation with a dry mechanical discharge and has, in addition, a low operating cost. For vacuum filtration, the capacity per sq. ft. per day is high, for the reason that the cake formed in these continuous filters does not exceed from ⅛ to ½ inch in thickness, and the time required for cake forming in any filter increases very rapidly as a thicker cake is made.

Oliver filters are very generally used in Mexico and the United States, and, numerically, probably head the list of filter plants in use in America.

At the Mexican Mill on the Comstock, a 11½-ft. by 16-ft. Oliver handles 80 tons daily, being 278 lbs. per sq. ft. per day. Operating costs are given as $0.072 and dissolved metal losses as $0.09, largely in silver.

The plant of the Minas del Tajo, in Sinaloa, with two 11½-ft. by 8-ft. Olivers, handles 100 tons, or 348 lbs. per sq. ft. per day. Caking effluent is given as $0.47 gold and 0.98 oz. silver, with a dissolved metal loss of $0.04 gold and 0.09 oz. silver. Operating costs are: Power, $0.0835; labor, $0.0161; supplies, $0.0227; total, $0.1223. At this plant the slime is settled and partly washed by intermittent decantation before going to the filters.

At the mill of the Nevada Wonder, where all operating charges are relatively high, the Oliver costs are given as: Labor, $0.106; power, $0.046; supplies, $0.038; and total, $0.19 per ton filtered. The capacity per sq. ft. of area is 270 tons per day.

The Portland Filter.

The Portland revolving-drum vacuum filter is similar to the Oliver in construction and operation. As a typical installation may be cited that at the Victor Mill of the Portland Gold Mining Company, where six filters, with a total filtering area of 2125 sq. ft., handle 300 tons, or 282 lbs. per sq. ft., per day. The total installation cost of this filter plant is given as $23,365.00, and operating costs are $0.08 per ton filtered. The caking effluent carries $1.25 in gold and the dissolved metal loss is $0.07.

Portland filters are also installed at the Cornucopia Mill in Oregon, where two 14-ft. by 9-ft. machines handle 228 lbs. per sq. ft. per day, with operating costs given as $0.081 per ton filtered.

PRESSURE FILTRATION.

Dehne Type Filter.

The Dehne type plate-and-frame pressure filters were the first machines used for the filtration of slime in the early days of the cyanide process, and many plants were installed, particularly in Africa and Australia. Working upon a granular or roasted slime, permitting three- and four-inch cakes, the washing with these presses is practically perfect, and charges are not excessive where labor is cheap. With amorphous slime, however, one- or two-inch frames must be used to obtain a solid cake, and even then the washing is erratic, with abnormal costs for labor and filter cloth, owing to the necessary frequent opening and closing.

Because of such defects, presses of this type have, in almost every case, been superseded by more modern equipment; two notable exceptions being certain districts in Australia and in Rhodesia, where a number are still in use, due mainly to the fact that by using a final air blow, residues may be discharged as low as 10% moisture—a vital point in these semi-arid districts.

The average cost of operating filter presses of the Dehne type in Australia may be taken as $0.25 per ton filtered, with an additional $0.10 for residue disposal.

The Merrill Filter.

The Merrill automatic sluicing filter introduces an entirely novel feature in the operation of plate-and-frame presses. A sluicing pipe extends throughout the length of the press and is provided with a nozzle projecting into each frame. For discharging, this sluicing pipe is slowly rotated, and jets of water at approximately 85-pounds pressure sluice out the cake through gates located at the bottoms of the frames.

This filter combines the recognized washing efficiency of the plate-and-frame press with a convenient mechanical wet discharge, and where water costs are not excessive, gives most satisfactory results. When the conservation of water is vital, the presses are sluiced into thickening tanks, where the water is recovered and re-used; the ultimate consumption in such cases seldom exceeding one ton per ton of slime filtered.

Two systems are used in operating these presses. Where the ore is comparatively granular and makes cake rapidly, the chambers of the press are filled solid full, and the wash or treatment solutions passed clear through the cakes. This requires a minimum amount of wash to effect displacement, frequently less than a 1 to 1 ratio, with attendant saving in precipitation and power charges.

When amorphous material is present in such amount as to cause the cakes to form and leach slowly, it is found preferable to discontinue filling when the chambers are almost, but not quite, full, and immediately to apply the wash or treatment solution through the pulp feed channels. Even with a high amorphous content, a rapid wash is thus obtained, since the cakes are from only one to one and one-half inches thick. Owing to a certain amount of diffusion between the wash and the residual filling pulp, a volume of wash solution equal to twice the weight of the ore is required.

Due to the nature of its construction, the capital cost of the Merrill filter is high, but in most cases this is more than offset by an unusually high washing efficiency and a low operating cost.

The largest installation of Merrill slime filters is operating at the Homestake, where 28—92-frame presses handle approximately 2000 tons per day. This is on the basis of a nine-hour

cycle and includes the total slime treatment. The capacity of the plant, if used for washing only, would approximate 8000 tons per day, with an operating cost as follows: Operating labor, $0.01; shop labor, 0.0015; power, 0.0005; canvas, 0.01; acid, 0.0046; miscellaneous, 0.0014; total, $0.028.

As typical of the operating cost of a large Merrill filter installation in Mexico, may be taken the following figures from the Esperanza Mining Company at El Oro. Approximately 1000 tons of slime are filtered daily with six presses, averaging 82 frames each, being equivalent to 100 pounds per sq. ft. per day. Caking effluent carries $3.20 in gold and one oz. silver. Dissolved metal loss is $0.03 in gold and 0.01 oz. silver. Operating charges are: Canvas, $0.0108; acid, 0.0035; labor, 0.02; miscellaneous, 0.0005; sluicing water, 0.0102; a total of $0.045 per ton filtered. The item for sluicing water represents all charges incidental to settling and returning for re-use all water sent out with sluiced residues.

As illustrating the additional dissolution of metal which almost invariably occurs during washing in pressure filters of this type, the following data from the Merrill installation at the mill of the San Luis Mining Company, in Durango, may be cited: The caking effluent carries 25 ozs. silver per ton, while re-washed filter heads and tails show 4.7 and 4.08 ozs., respectively, an extraction of 0.62 oz. thus taking place during filtration.

The Kelly Filter.

The Kelly enclosed-leaf pressure filter is in use in several plants in Mexico and the United States, in particular in those where a dry discharge is desired, but its use has not extended largely to foreign countries.

The operation of this filter involves the return, at each cycle, of excess pulp and excess wash to their respective tanks, and, in conjunction with the frequent opening and closing for discharge, results in operation and maintenance charges somewhat higher than the average. The successful operation of this filter would also seem to be more than usually dependent upon skilled operators. Under certain conditions, however, these points may be more than offset by the advantages of a comparatively dry residue.

Five 5-ft. x 14-ft. Kelly filters at the mill of the Tigre Min-

ing Company, in Sonora, handle 250 tons of slime daily, being at the rate of 83 lbs. per sq. ft. per day, with an operating cost of $0.25 per ton.

A 4-ft. x 10-ft. Kelly filter at the 50-ton Iola mill, in North Carolina, handles 50 tons in 12 hours, or 475 lbs. per sq. ft. per day. No solution wash is used in the 30-minute cycle. The loss in dissolved value averages 7c, ranging up to 15c. Operating cost, exclusive of power, is given as 8.5c.

The Burt Filter.

The Burt revolving pressure filter is one of the most ingenious machines developed for slime filtration, but, unfortunately, the small filter area obtainable in each machine has restricted its use to very granular slime. On such material, it is capable of giving a very perfect wash, and will discharge with a small amount of water. The filter was developed at El Oro, Mexico, and is in operation in the mills of the El Oro Mining and Railway, and the Mexico Mines of El Oro.

At the former plant, fourteen 42 in. x 40 ft. filters handle 1200 tons daily, or 410 lbs. per sq. ft. per day, with cake 4 to 6 inches in thickness. The slime is unusually granular and is partly washed by decantation before going to the filters. Operating costs are: Labor, $0.014; power, 0.011; supplies, 0.024; total, $0.049. The washing efficiency is stated to be 98%.

CONTINUOUS COUNTER-CURRENT DECANTATION.

This method of separating dissolved values from treated slime, by means of a series of Dorr continuous thickeners, is becoming very popular in America, particularly in small plants, and more especially in those treating a granular product, which readily settles to 40% moisture or less and is amenable to treatment with very low cyanide strengths.

In operation, the slime passes through a series of tanks, the thick underflow of each being diluted with solution overflowing the second following thickener of the series. The solids thus move constantly in one direction, while the solutions travel in the opposite direction. Water, in quantity sufficient to replace the moisture finally discharged with the tailing, is added at the final thickener. The solution, traveling successively toward the head of the series and mixing with

constantly richer pulp, is finally used in the crushing department, from whence it overflows the first, or primary, settler and is sent to precipitation. The tanks are generally set so that solutions gravitate throughout the series, and the necessary elevation of the thick underflow is made either with diaphragm pumps or with air lifts.

In most plants where continuous decantation has been successfully used, underflows of 35 to 40% moisture are usually maintained and solution equal to from 4 to 6 times the weight of the ore is clarified and precipitated. Under these conditions, the recovery of dissolved metals is excellent, but the loss of cyanide is higher than with filters.

This mechanical loss of cyanide is recognized as one of the principal factors limiting the use of continuous decantation without filters, where even moderately strong solutions are used. Solutions of less than ½ lb. KCy are seldom precipitated in American practice, and at this strength, the mechanical loss in the final residue will vary from ¼ lb. to as high as 1 lb., depending on underflow moistures. In milling silver ores, there will be an additional loss, owing to the fact that dissolution of the metal continues as long as the slime is in contact with solution.

The actual operating cost of the thickeners is very low, and the simplicity of the plant, enabling labor and supervision to be reduced to a minimum, must appeal strongly to operators of small plants.

As a most interesting adaptation of continuous decantation and vacuum filtration, may be cited the practice at the recently enlarged Hollinger mill at Porcupine. Small thickeners, operating as classifiers, separate the tube-mill product into amorphous and granular. The former is thickened and sent to a vacuum filter for washing, without other agitation than that obtained in grinding, pumping and thickening.

The granular portion is concentrated, thickened, agitated, and then sent to counter-current decantation tanks for washing. This system eliminates amorphous or colloidal material from the bulk of the tonnage, where a very thick underflow is imperative, and, at the same time, furnishes a satisfactory product for the filter.

The following data on counter-current decantation appears in Maurice Summerhayes' article on the Porcupine Crown Mill (Min. & Sci. Press, July 18, 1914). At this plant counter-current washing is carried out in four settlers in series, underflows of 30 to 35% moisture being regularly obtained. Daily ore tonnage is 120, and 4.06 tons of solution are precipitated. The solution going to the first of the washing thickeners carries $1.74, and the overflow of the final thickener, $0.10. Loss in dissolved gold is $0.043 per ton milled, total KCy consumption being 0.74 lbs., of which 0.32 lbs. is mechanical loss.

Operating costs for April, 1914, are given as follows:

	Wages	Material	Power	Total Cost Per Ton
Solutions	$208.11	$422.86	$24.97	$0.18
Precipitation	128.96	292.50	24.75	0.12
Thickeners	215.72	4.21	67.35	0.08
Clarifying	110.56	.....	.....	0.03
Agitation	120.95	.....	.....	0 04
Refining	271.08	92.11	.....	0.10
Total				$0.55

Thus the cost of dissolution and counter-current washing approximates $0.30 per ton, with clarifying, precipitation and refining at $0.25 per ton.

Intermittent Decantation.

This process, although the first effective solution of the slime treatment problem, is now confined almost exclusively to Africa. Its continued use on the Rand is due to several factors, the chief of which are the remarkably low solvent strengths necessary to effect dissolution, and the ability to precipitate solutions containing only 0.15 lbs. of cyanide per ton. Of equal importance, as already pointed out, is the remarkably complete settling normally obtained.

Tanks seventy feet in diameter by twelve feet deep are commonly used in the larger plants, with transfer pumps which handle a charge of 1800 tons of pulp in from 60 to 90 minutes. Two decantations are usually given, one in the treatment tank and one in the washing tank. A third decantation is added in special cases. The volume of solution precipitated is from three

to four tons per ton of slime handled, the cyanide strength averaging from 0.005 to 0.01% in KCy.

Since the operations of dissolution and washing are here so closely linked, separate costs of the two operations are not obtainable. In discussing the Butters filter on the Rand, the writer has already brought out the relative costs of decantation and filtration plants. Unquestionably, the weakest point in decantation, as practiced on the Rand, is the liability to serious loss, due to poor settling and imperfect precipitation during the winter months. This danger is largely, but not entirely, obviated by the use of filters. In this connection, it should be borne in mind that all the Rand plants have an important safety factor, in that part, at least, of the dissolved value sent to the residue slime dams is recovered in the operation of the return-water system.

CONCLUSION.

Unquestionably, the handling of slime, as produced from the operation of the cyanide process, has reached a point where no further radical changes should be expected. The operation of separating the dissolved metal from the treated residue may now be carried out at a cost of $0.05 per ton, under favorable conditions, and recoveries of 98 and 99% are not at all unusual. The mechanics of the various machines will, of course, be modified and improved to suit the needs of special problems, and there is always the possibility of reducing capital cost. In comparison, however, with the development of the last ten years, these further modifications will be relatively unimportant.

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7 Sand, Slime and Colloids in Ore Dressing. G. Caetani, Mar. 22, 1913.
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7 Trent Agitators at West End Mill, Tonopah, Nevada. J. A. Carpenter, May 3, 1913.
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7 Filter Pressing—Kalgoorlie. M. W. von Bernewitz, Sept. 17, 1910.
7 Operation of the Oliver Filter in the Globe Mill. H. A. Morrison and H. G. Thomson, Oct. 10, 1914.
6 Burt Revolving Pressure Filter. C. E. Rhodes and A. B. Meyers, June 13, 1914.
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9 Vacuum Slime Filtration (Butters). H. F. Julian, Oct., 1911.
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DISCUSSION

Mr. Butters.

Mr. Chas. Butters,* Mem. Am. Inst. M. E., expressed the opinion that developments would take place in the future which would greatly accelerate the settling of slime. He also expressed the idea that it might be possible in the future to construct a filter that would not only separate solids from liquids, but dissolved salts as well.

* Oakland, Calif.

Mr. DuRell.

Mr. C. T. DuRell,† Mem. Am. Inst. M. E., called attention to the difficulty at times encountered in connection with the settling of slime. He advanced the theory that this was largely due to entrained air in the slime floes, so that instead of settling, the process of flotation was being stimulated. He said that colloids have been frequently blamed for this trouble, but that, in his opinion, air is the real culprit. He also thought that with improvements in settling, filtration would be unnecessary.

Mr. Oliver.

Mr. E. L. Oliver,§ Mem. Am. Inst. M. E., stated that in the giving of cost data in a paper of this kind, a unit system should be adopted; for instance, the cost of labor is given for certain operations, but the labor may cost $4 per day or it may cost $1 per day.

† Los Angeles, Calif.

§ San Francisco, Calif.

Paper No. 188

PRECIPITATION.

By.

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Professor of Metallurgy
Leland Stanford Jr. University, Calif., U. S. A.

Since the inception of the cyanide process it has been the ambition of inventors to accomplish the operation of precipitation in conjunction with that of solution. The Pelatan-Clerici process at the De Lamar Mine, Idaho, and the Gilmour and Young process at the Santa Francisco Gold Mine, Nicaragua, were examples of such processes which met with a certain degree of success. Neither process has been in operation for a number of years. Numerous attempts have been made to precipitate gold and silver dissolved in cyanide solutions electrolytically from ore pulps upon metallic plate cathodes; but, when the difficulties of electrolytic precipitation from clear solutions are recalled, it is not surprising that with the added difficulties due to the presence of the ore these attempts should have failed. One of the supposedly strong points of such a process is the possibility of dispensing with filtration; but, even if a reasonable degree of success be conceded to the process, filtration or some other effective method for separating the waste solids from the solution must be practiced if the solvent is recovered, and, as recovery of the solvent is of vital importance to the economical operation of the cyanide process, there would appear to be nothing to be gained by incurring the greater difficulty of attempting to precipitate gold and silver from the pulp rather than from the separated solution.

In present day practise, the solution is invariably separated from the waste solids before precipitation is attempted.

In the past, it has been argued that complete removal of the suspended matter from the solution is not essential to good precipitation and that, inasmuch as sand is generally added to the precipitate as a flux before melting, it is a useless refinement to clarify solution before precipitation. However, it is now generally conceded that suspended matter in the pregnant solution interferes with efficient precipitation, on account of preventing proper contact of the solution with the precipitant. Furthermore, the light flocculent solids remaining in suspension in the solution are the most refractory portions of the ore. Instead of functioning as a useful flux, they actually cause a greater consumption of fluxes and, in general, add difficulty to the melting operation. It may, therefore, be taken as axiomatic that only clear solution should be precipitated.

The solutions resulting from sand leaching are, in general, sufficiently clear for precipitation, but the solutions resulting from slime treatment carry more or less solid matter in suspension and require clarifying before precipitation. When combined sand and slime treatment is used, a considerable proportion of the pregnant solution resulting from slime treatment can be advantageously clarified and built up in value by using it as the first washes upon the sand. But the sand plant cannot be entirely depended upon for clarifying the slime-plant solution; hence, even when there is a sand plant, auxiliary means for clarification should be provided.

The oldest and perhaps the simplest type of clarifying device is a tank arranged for leaching, filled preferably with rather coarse waste sand. The layer of slime formed on top of the sand, which gradually causes the leaching rate to decrease, is removed at frequent intervals, or the whole of the sand is removed, washed and replaced. Frequent attention is essential if the original capacity is to be maintained. Clarifiers of this type have, at times, served their purpose, but they are cumbersome, of relatively small capacity, and require considerable labor.

Various adaptations of the leaf filter, either operated by gravity or vacuum, have also been used.

An expedient which is sometimes used in conjunction with zinc shaving precipitation is to fill the head compartments of

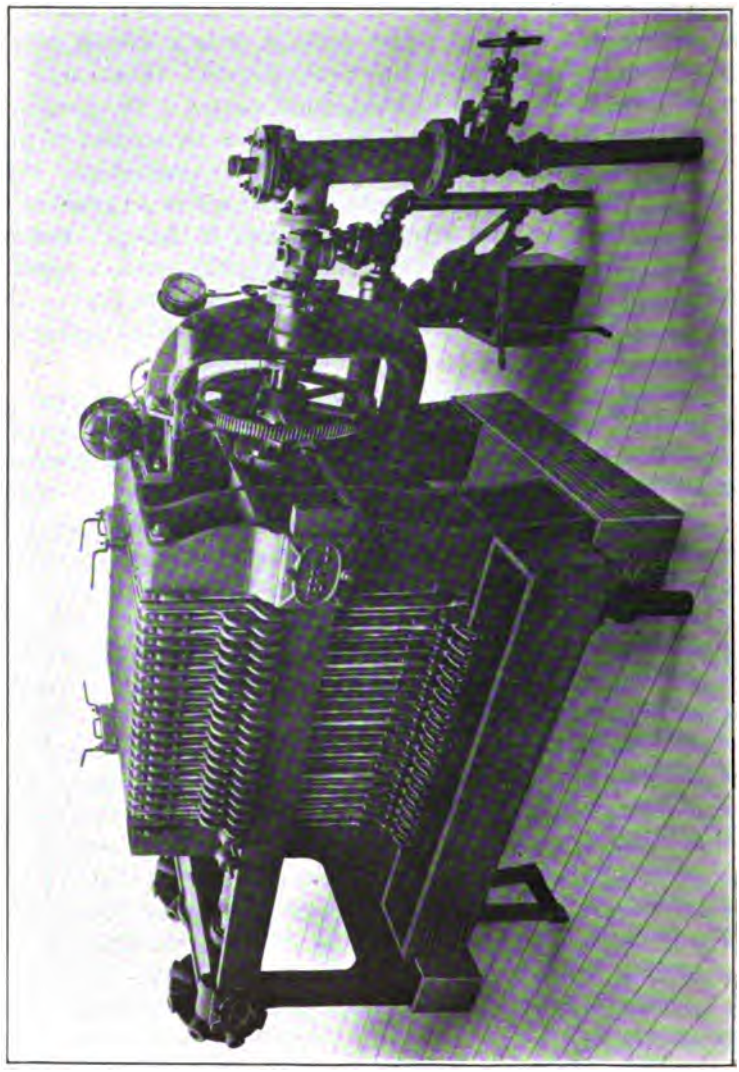


Fig. 1. Latest Model of Merrill Clarifying Press.

the box with excelsior or other fibrous material. This must be removed at frequent intervals and washed.

At the present time, the Merrill clarifying filter press presents the highest development in clarifying devices. The improved model is shown in Figs. 1 and 1A. It will be noted that it is an adaptation of the plate and distance frame type of filter press so arranged that the solids may be discharged from the chambers and the cloths washed without opening the press.

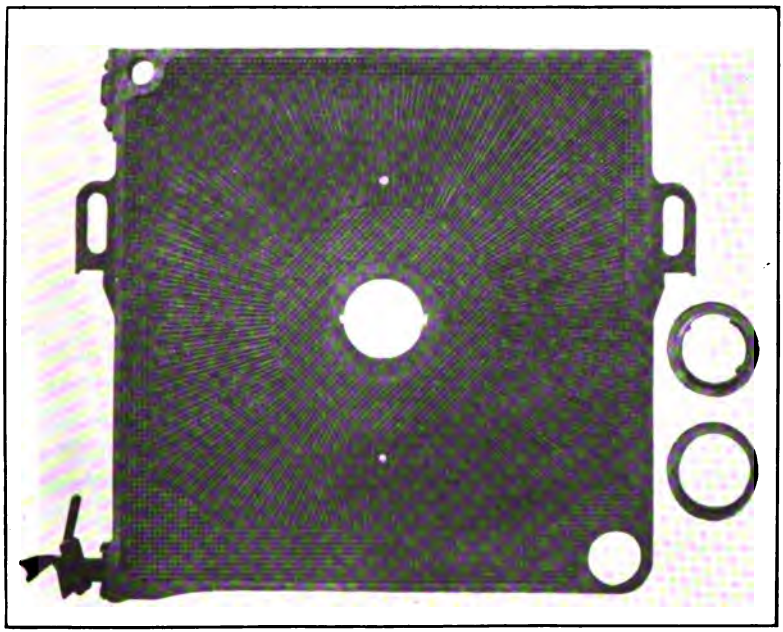


Fig. 1A. Filter Plate of Clarifying Press.

In this model the frames are made one inch in thickness, just sufficient for properly introducing the sluicing nozzle. The manually-operated sluicing bar located at the bottom of the frames of the earlier type has been replaced by a motor-driven bar located at the center of the frames. These changes have resulted in a compact machine which uses the minimum of sluicing water. The criterion of capacity of clarifying devices is the number of square feet of filtering surface. The number

of square feet of filtering surface required per ton of solution clarified per twenty-four hours depends, in any particular case, upon the nature and amount of solids to be removed from the solution. Costs are also quite variable, depending to a considerable extent upon local conditions. Results are, therefore, given for two rather widely separated mills, which may be taken as indicative of general practise.

At the Hollinger Mill, Porcupine, Ontario, Canada, treating 500 tons of ore per day, 1500 tons of solution are clarified by two 20-frame 36-inch clarifiers (a total of 560 square feet of filtering area). Each clarifier is sluiced every 8 hours. Below are given detailed costs of clarification at this plant:

	Per ton of ore	Per ton of solution
Power for pumping at $50.00 per hp.-yr.	0.224 cents	0.074 cents
Canvas	0.028 "	0.009 "
Acid treatment	0.044 "	0.015 "
Total	0.296 cents	0.098 cents

No charge is made at this plant for labor, as the number of men employed in the mill is not increased by the clarifiers.

At the Portland Mill, Colorado Springs, Colorado, U. S. A., treating 350 tons of ore per day, 1200 tons of solution are clarified by one 30-frame 36-in. clarifier (420 square feet of filtering area). The clarifier is sluiced every 4 hours. Below are given detailed costs of clarification at this plant:

	Per ton of ore	Per ton of solution
Operating labor	0.13 cents	0.038 cents
Repair labor	0.12 "	0.035 "
Acid treatment	0.07 "	0.021 "
Power	0.40 "	0.116 "
Lights	0.02 "	0.005 "
Total	0.74 cents	0.215 cents

No charge is made at this plant for filter cloth, as discarded cloths from the slime presses are used for the clarifying press.

CLASSIFICATION OF VARIOUS METHODS OF PRECIPITATION, USED AND PROPOSED.

- **Electrolytic**
  - (a) Iron anode; lead cathode; low current density; adherent deposit.
  - (b) Peroxidized lead anode; tin plate cathode; high current density; non-adherent deposit.
  - (c) Peroxidized lead anode; lead plate cathode; high current density; adherent deposit.
  - (d) Indirect electrolytic processes (Have only been investigated experimentally).
- **Chemical**
  - Gaseous — Only example; possibly occluded gases in charcoal.
  - Liquid — Sodium sulphide (Proposed for precipitating silver). Cuprous salts in acid solution.
  - Solid
    - Non-metallic — Charcoal
    - Metallic
      - Sodium — In form of amalgam, generally produced by electrolysis
      - Aluminum — Shaving, Dust
      - Zinc — Discs, Shaving, Dust

Electrolytic Precipitation.

A cyanide process of ore treatment involving electrolytic precipitation was invented by Dr. Siemens at about the same time that MacArthur and Forrest invented their cyanide process involving zinc-shaving precipitation. However, little was done with electrolytic precipitation until the problem of precipitating the solutions resulting from slime treatment arose in South Africa, through the inability of zinc shaving precipitation, as then practiced, to cope with such solutions. In the Siemens-Halske process, as practiced in South Africa, the wooden containing box, although larger, had the same general arrangement as the boxes used for zinc-shaving precipitation, i. e., wide compartments containing the iron anodes and lead-foil cathodes through which the solution had an upward flow, alternated with narrow compartments which only served for the downward flow of the solution. A low-current density was employed, resulting in a coherent deposit. The gold was recovered from the foil cathodes by cupellation.

The introduction of the lead couple and a drip of strong solution, which is not always used, rendered zinc-shaving precipitation satisfactory upon dilute slime solutions. Following this improvement in zinc-shaving precipitation, there was a long and bitter controversy regarding the relative merits of the two methods of precipitation for slime solution, since electrolytic precipitation never had been much favored for precipitating the stronger solutions resulting from the treatment of the sand. The final result was that electrolytic precipitation was entirely displaced by modified zinc-shaving precipitation. Later, Chas. Butters, who had been identified with the introduction of the Siemens-Halske process into South Africa, adopted electrolytic precipitation for mills in which he was interested at San Sebastian, Salvador, Minas Prietas, Mexico, and Virginia City, Nevada, U. S. A., largely on account of the possibility of the interference with zinc-shaving precipitation of the copper present in the material to be cyanided. An entirely new practice was evolved, which, at least upon the material treated, seemed to present certain advantages over the Siemens-Halske process. The changes inaugurated at the outset, or later developed, consisted of the use of a peroxidized lead-plate anode, a tin-plate cathode and a sufficiently high current density to give a non-coherent deposit, the idea being to collect the precipitated metals as a sludge at the bottom of the box, as in zinc-shaving precipitation. The electrolytic precipitation box, used at Virginia City, is shown in Figure 2. At San Sebastian this practice was modified to the extent of substituting a lead plate for the tin-plate cathode. Although the current density was higher than any of the other plants where the predominant metal precipitated was silver, on account of the solutions containing only gold with copper as the predominant metal, a coherent deposit was obtained. The copper and gold were separated from this deposit by an ingenious method of electrolytic refining, which has been described elsewhere. A small installation closely following the Butters practise was installed and in use a short time at the El Rayo Mine, Mexico. With the exception of Minas Prietas, these plants followed electrolytic precipitation with zinc precipitation for all the solution which they wished to render entirely barren for final washes. Eventually, in all

of these plants electrolytic precipitation was superseded by zinc precipitation. This was possible on account of the changes in the character of the material treated, as well as through a more thorough understanding of the possibilities of zinc precipitation.

The following table on page 370 gives the essential features commercial electrolytic precipitation as practiced in the past at various plants.

Both the cost of installation and operation of electrolytic precipitation are higher than zinc precipitation. In South Africa, it has been estimated that the cost of a Siemens-Halske plant for precipitating the solution from a 500-ton slime plant would be $12,537.11, while a zinc-shaving plant for using the lead couple would cost $2,128.44.

Six standard electrolytic precipitation boxes, at Minas Prietas, Mexico, cost $20,005.00, while six standard boxes of somewhat more elaborate design, at Virginia City, Nevada, U. S. A., cost $18,503.00.

Minas Prietas was the only plant upon the American continent to use electrolytic precipitation exclusively. I am indebted to Mr. M. F. Perry for the average cost of operation covering a period of six years:

Power	$0.083
Labor	.037
Supplies	.031
Depreciation	.040
Total per ton of ore	$0.191

One of the great problems of electrolytic precipitation is the formation of by-products, which invariably contain the precious metals. These are largely the result of disintegration of the anodes. Despite the disadvantages of electrolytic precipitation, there are possibly cases which may arise, where there is considerable base metal to deal with, when it would be the only resort. It is also possible that certain of the difficulties of electrolytic precipitation may be eventually overcome.

Process	Location	Number of Plants	Anode	Cathode	Current Density per sq. ft. Anode amperes	Voltage	Metals in Solution	Remarks
Siemens-Halske	Rand, South Africa	20	Iron	Lead foil	0.03 to 0.06	4 to 8	Gold	Used alone.
Butters-Andreoli	Minas Prietas, Mexico	1	Peroxidized Lead	Tin plate	0.30 to 0.55	2.6 to 3	Silver, Copper, Gold	Used alone.
Butters-Andreoli	San Sebastian, Salvador	1	Peroxidized Lead	Lead plate	1.00 to 1.20	3 to 3.5	Copper, Gold, Zinc	Followed by zinc shaving.
Butters-Andreoli	Virginia City, Nevada	1	Peroxidized Lead	Tin plate	0.25	2.87	Silver, Copper, Gold, Zinc	Followed by zinc shaving.
Butters-Andreoli	El Rayo, Mexico	1	Peroxidized Lead	Copper foil	1.20		Silver, Copper, Gold, Zinc	Preceded by zinc dust.

Charcoal.

The use of charcoal as a precipitant has been almost exclusively confined to the Victoria District of Australia. Wm. Davis found in chlorination that 12.46 parts of charcoal were required per 1 part of gold precipitated, while John I. Lowles states that at one Victorian cyanide plant, 208.3 parts of charcoal were required for 1 part of gold. This shows very clearly the lower efficiency of charcoal when used with cyanide solutions. The exact action of charcoal in precipitation is unknown but its behavior as a precipitant is generally attributed to occluded gases, carbon monoxide, hydrogen or hydrocarbons. Charcoal which has become inactive through use as a precipitant again becomes active upon heating. This is probably due to the formation of carbon monoxide in the pores of the charcoal.

The weak points of charcoal precipitation are the enormous surface necessary for efficient precipitation and the practical difficulties encountered in recovering the gold from the large bulk of charcoal. One very interesting, and to my mind important, peculiarity of charcoal is that the weaker the solution the more favorable it is for precipitation. This is just the reverse of zinc precipitation. The most difficult condition for zinc precipitation to meet is a solution containing but a trace of cyanide. If the general principle of precipitation with occluded gases could be applied in a more efficient manner than in charcoal precipitation, it would appear to offer a possible solution of the perplexing problem of precipitating unusually dilute solutions.

Aluminum.

Aluminum was originally proposed as a precipitant by Moldenhauer, more than twenty years ago, but it was not until applied in the form of dust by Kilpatrick, in 1908, at the plant of the Deloro Mining and Reduction Company, for precipitating high-grade silver solutions, that it became a commercial success. Later it was adopted by the O'Brien Mill and the Nipissing Mills, in the Cobalt District, for precipitating low-grade silver solutions.

Aluminum-dust differs from zinc-dust precipitation in that violent agitation is necessary to wet it and a longer period of

contact with the solution is required. This end is accomplished at the Deloro and O'Brien plants by means of a vortex agitator, as shown in Fig. 3. At the Nipissing Mill a simpler form of agitator, as shown in Fig. 4, has been found effective. It is also essential that caustic soda be present in the solution, and lime avoided as far as possible.

Estimated comparative costs of zinc and aluminum-dust precipitation indicate that, unless credit be given for a saving

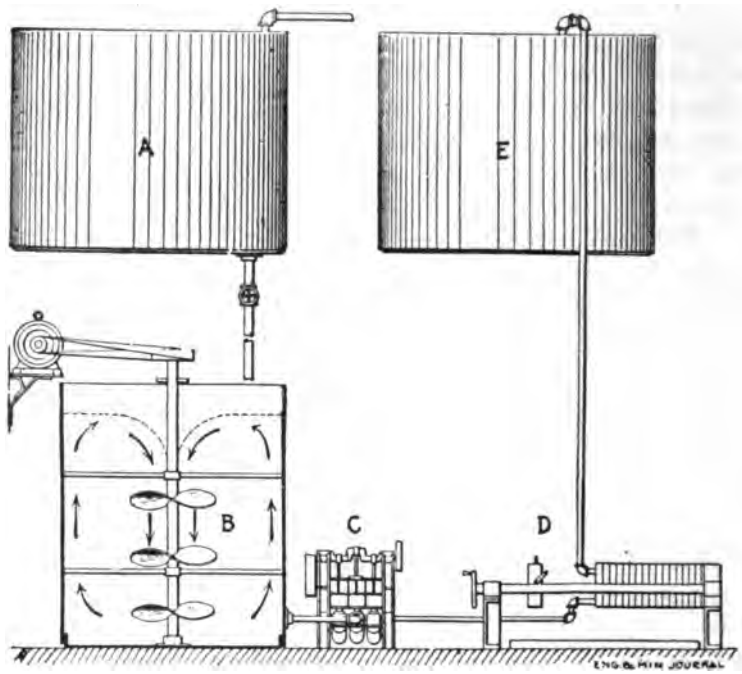


Fig. 3. Aluminum Dust Precipitation.

in cyanide, the cost of aluminum precipitation would, in general, be greater. However, a lowering of the cost of aluminum dust or a rise in the cost of zinc dust might give aluminum dust the advantage.

The superior regeneration of cyanide has been claimed as a distinct advantage for aluminum precipitation, but this contention has never been proven by working-scale parallel tests with zinc precipitation upon the same ore. An equivalent weight of

aluminum is very much more efficient than zinc, both theoretically and practically, but this advantage may be offset by the higher cost of aluminum dust. As the presence of caustic soda is absolutely essential, aluminum precipitation cannot be used when caustic soda in the solution is harmful. But, on the other hand, any appreciable amount of caustic soda in solution is harmful in all forms of zinc precipitation. When caustic soda is beneficial to extraction, other conditions being favorable, aluminum precipitation could be used to advantage. This

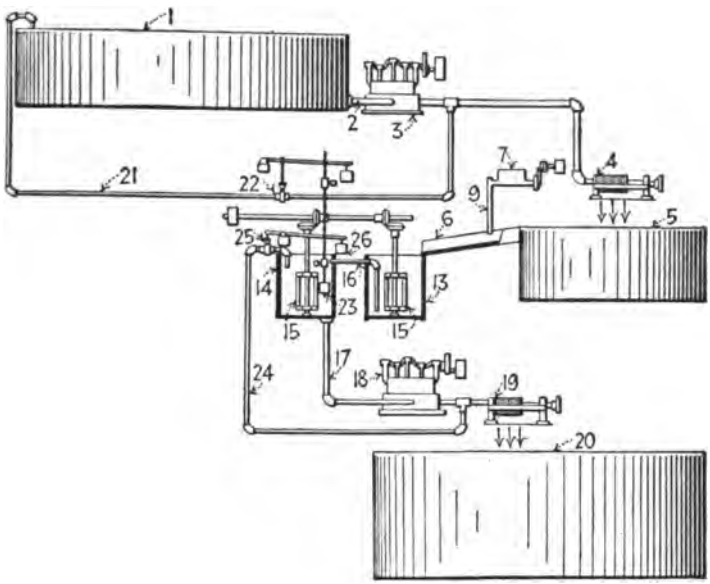


Fig. 4. Aluminum Dust Precipitation.

is also true when there are elements in the ore, as for example, arsenic, which are dissolved by the solution and which, in the presence of zinc, interfere with extraction. Zinc dissolved during precipitation may perform the useful function of keeping the solution free from various deleterious substances, as for example, soluble sulphides, but aluminum in solution is of no value for this purpose.

So far as I am aware, there have been only three commercial installations of aluminum-dust precipitation and these have

been used for precipitating silver solutions. There are, therefore, no data regarding its behavior upon a working scale with gold solutions. Small-scale tests seem to indicate that it would not be as satisfactory for this purpose as zinc dust.

Zinc Shaving.

Zinc shaving, the earliest used commercial precipitant, is still an important method of precipitation. The general principle of dividing a rectangular box or arranging individual units so that there are alternate wide and narrow compartments, the wide compartments containing the zinc shavings, supported upon suitable screens, serving for the upward flow of the solution, with the narrow compartments merely serving for the downward flow of the solution, has never been departed from in zinc-shaving precipitation. The tendency in recent years has been to decrease the number but to increase the size of the compartments. Both wood and sheet steel have been used in the construction of precipitation boxes. The difficulty of making this particular form of construction in wood so that it will not leak has led to the very general use of steel for this purpose. Steel has at times been condemned on account of the fact that it forms a galvanic couple with the zinc, which causes a greatly increased zinc consumption. This would, perhaps, be true if the steel remained bright, but it is customary to protect steel boxes by a protective coating of inert asphaltic paint and, furthermore, after the boxes have been in operation for a time, a deposit of lime scale forms, which is quite an effective coating. In precipitating solutions containing silver, it sometimes happens that the interior of a steel box becomes silver plated. This phenomenon is not entirely under control, but when it occurs, it forms excellent protection for the iron.

A generally accepted figure for zinc-box capacity has been to provide one cubic foot of zinc for each ton of solution precipitated per twenty-four hours. However, if the boxes are given the proper attention, this figure is higher than is necessary. It is obvious that, if little attention is to be paid to the packing of the boxes, a larger volume of zinc must be provided to mitigate the evils of channeling. On the other hand, with very frequent packing, satisfactory results may be attained with a very small zinc-box capacity; but perhaps at the

expense of a somewhat increased zinc consumption on account of the extra handling. Below are given the essential features of zinc-box precipitation at a number of widely separated plants:

Details of Zinc-Shaving Precipitation.

Name of Plant	Type of ore	Size of compartments	Cu. ft. of zinc per ton of solution precipitated per 24 hours
San Rafael, Pachuca, Mexico	Silver-gold	33" x 33" x 30"	
Loreto, Pachuca, Mexico	Silver-gold	36" x 48" x 30"	0.75
Dos Estrellas, El Oro, Mexico	Silver-gold	30" x 30" x 24"	0.65
El Oro Mining & Railway, El Oro, Mexico	Gold-silver	36" x 48" x 24"	
Guanajuato Consolidated, Guanajuato, Mexico	Silver-gold	36" x 48" x 18"	0.40
Guanajuato Reduction & Mines Co., Guanajuato, Mexico	Silver-gold	48" x 48" x 30"	1.06
Divisadero, San Salvador, Central America	Silver-gold	24" x 36" x 18"	0.54-0.81
Golden Cycle, Colorado Springs, U. S. A.	Gold	48" x 24" x 24"	0.56
Tonopah Extension, Tonopah, Nev., U. S. A.	Silver-gold	30" x 34" x 26" 36" x 34" x 30"	0.93

The manner of packing the compartments is of importance. In the United States, where labor is high, the shaving is generally introduced in tangled masses, just as it is collected from the lathe, only sufficient attention being given to the boxes to insure low tail solutions. In Mexico and certain other countries where labor is cheap, it has been found advantageous to pay more attention to the detail of the manipulation of precipitation boxes. At the El Oro plant, a number of years ago, the skein method of packing was developed.

This was adopted at a number of other plants in Mexico. The shaving is made into skeins 3 to 5 inches in diameter and of such a length as to reach from one side of the compartment to the other. In case that the compartment is rectangular, it is necessary to make half the skeins the length of the short dimension and the other half the length of the long dimension. The skeins are formed by a boy who winds the shavings, as they come from the lathe, onto a reel. In packing the compartment, a layer of skeins is closely laid upon the screen at the bottom, the next layer is laid at right angles to the first, and so on until the compartment is full. Fig. 5 shows a typical wooden precipitation box packed in this manner. This results

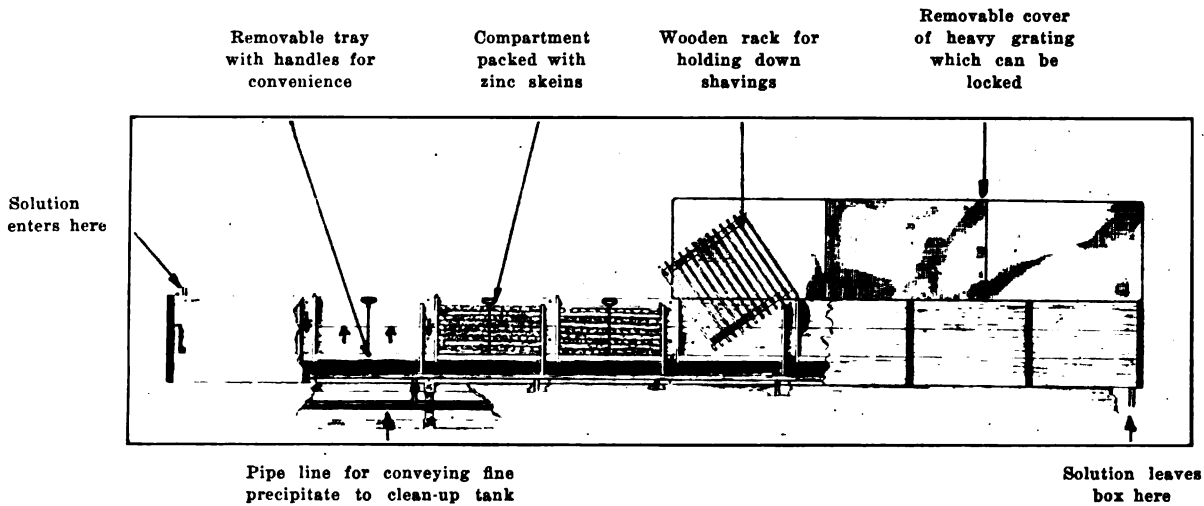


Fig. 5. Typical Wooden Precipitation Box.

in a uniform and compact mass of zinc shaving which does not unduly retard the flow of the solution. To attain the full benefit of the skein method, it is necessary to remove all the skeins from the compartments and repack as soon as the slightest channeling is evident. Herein lies a danger, for the precipitate upon the surface of the zinc forms a powerful catalytic agent which induces rapid oxidation of the damp zinc shaving when exposed to the air. This action goes on so rapidly at times that a pile of coated shaving which has been exposed to the air during the interval of packing a compartment will become quite hot. When packing zinc boxes, partially used zinc should at all times be kept under the solution. It is, therefore, good practice to keep one empty compartment near the center of the box for this purpose. In general, on account of breaking and oxidation, the less the zinc is handled, consistent with the prevention of channeling, the better.

The two bugbears of zinc-box precipitation are "short zinc" and "white precipitate". The short zinc is ever present, while the white precipitate is an occasional malady. The short zinc is the result of the breaking of the partially decomposed shavings. Formerly, when acid treatment of the precipitate was practised, it was disposed of by treating with acid; but, since acid treatment of the precipitate has been abandoned in the majority of plants treating silver ores or silver-gold ores, other methods for its disposal have been adopted. A simple, but perhaps not always effective, method is to pack the short zinc with the fresh zinc added to the head compartments. This means considerable handling of zinc, which is, of course, objectionable. The equipment of one or more of the head compartments of the precipitation boxes with a series of superimposed shallow trays, upon which the short zinc is placed as rapidly as removed from the boxes, has proven satisfactory in most cases. "White precipitate" not only interferes with precipitation on account of coating the zinc but also lowers the grade of the precipitate. Generally, it is the result of the lowering of the concentration of the cyanide to a point where certain of the dissolved salts are thrown out of solution and, as might be expected, is most frequently encountered when precipitating weak solutions. Although of variable composition,

the most effective remedy is the addition of cyanide. Various couples of zinc with other metals have been proposed and tried as precipitants, but the only couple which has been commonly used is lead. All commercial sheet zinc contains upwards of 1% of lead; therefore, the lead couple is involved to a slight extent at all times in zinc shaving precipitation. The lead couple produced intentionally by the immersion of the zinc shaving in solutions of lead salts is now only used for precipitating very dilute solutions, which are difficult if not impossible to precipitate by other methods. Its present use is, therefore, almost exclusively confined to South Africa for precipitating gold from the dilute solutions resulting from slime treatment. It is also useful when precipitating solutions containing copper. The zinc-lead couple is only effective for a very short time, when it must be removed and replaced by freshly-dipped zinc shavings. This would constitute a heavy consumption of zinc but for the fact that the inactive precipitant can be satisfactorily used for precipitating stronger solutions.

Preparation of Zinc Shavings.

The proper preparation of the zinc shaving is a matter of vital importance in this form of precipitation. In order to increase the surface and render the shavings more uniform, it has from the first been the practise to cut the shavings from a mass of sheet zinc, suitably held together, rather than from a solid zinc casting. The thickness of the shavings depends upon the solutions to be precipitated. The general practise in precipitating gold solutions where the maximum surface is desirable is to use a thin shaving, approximately 1/500″ thick. When silver predominates, thicker shavings are employed to advantage. The earliest form of zinc lathe was merely an arbor similar to those used for mounting emery wheels. The sheet zinc, cut in the form of discs about 12 inches in diameter and having a hole cut at the center to accommodate the shaft, was clamped in the arbor. The shavings were cut by means of a hand chisel, generally made from an old file, after the fashion of ordinary wood turning. The results obtained depended much upon the skill of the operator. At best, the capacity was small, the product not uniform, and usually there was considerable waste. The next development was to form a bundle of

zinc by winding sheet zinc upon a wooden or steel mandrel. This was mounted in an ordinary screw-cutting lathe and the shavings cut from the end of the bundle. This resulted in considerable improvement, but the ordinary screw-cutting lathe, unless of heavy construction and specially modified for this service, is not entirely satisfactory. The earlier types of specially-built automatic lathes were not built heavy enough and had no arrangement for cooling; therefore, they could not always be depended upon to give continuous service. Zinc varies from an extremely brittle metal to a comparatively malleable one, depending upon the temperature. As considerable heat is developed during the cutting of a thick mass of zinc, it is evident that means for cooling to the most advantageous temperature should be provided. Cooling is also necessary to prevent superficial oxidation of the shavings.

Recent improvements in automatic zinc-cutting lathes have been along the lines of making them much stronger and more rigid and also providing proper provision for cooling. It is now the general practise in America to cool the mandrel by circulating water through it. A plant in Mexico City for the commercial production of zinc shavings has carried cooling to the extent of circulating brine from a refrigerating machine, at -3° centigrade, through the mandrel of the lathe.

Another method of cooling has been to use a drip of water upon the cutting tool. This practise is condemned by some operators, as it may lead to oxidation of the zinc, and, when employed, the shavings should be used as soon as possible. In South African practise, heavy lathes are used, but there does not appear to be the care taken regarding cooling that is commonly observed in this country. The mandrels used hold 400 to 500 pounds of sheet zinc. A lathe is capable of cutting 30 to 33 1/3 pounds of zinc shaving 1/500 inch thick per hour.

At present the highest development in the art of zinc-shaving production has been attained by the Braun Corporation of Los Angeles, California. This company uses two lathes which were specially designed and built to their order. Each weighs 3000 pounds and is mounted upon a special concrete foundation. The essential features of this lathe are shown in Figs. 6, 7 and 8. The mandrel holds 1800 pounds of sheet zinc,

Fig. 7. Loading Mandrel of Lathe with Sheet Zinc.

Fig. 8. Lathe Cutting Zinc.

and each lathe cuts 83 1/3 pounds of zinc shavings 1/500 inch thick per hour. Aside from their size and the fact that a cut is taken simultaneously from each end of the zinc roll, the novel feature of this machine is the special method of cooling the mandrel, which is a hollow cast-iron drum, 24 inches in diameter. On the inner surface of the drum is a series of circumferential ridges, or fins, for dissipating the heat. The heat is carried away from the drum by means of an air current (produced by a small blower) which enters at one end of the drum through one of the hollow supporting trunnions and makes its exit through the other trunnion. The dissipation of the heat is further aided by introducing with the air a spray of water, so adjusted that most of the water is evaporated. The shaving made with this lathe is of uniform size and shows no evidence of oxidation. It is, therefore, evident that, with proper provision for cooling, the capacity of zinc lathes may be greatly increased.

Zinc Wafers.

MacArthur, who was instrumental in introducing zinc shaving as a precipitant, has recently described the zinc-wafer method of precipitation. The compartments of an ordinary zinc-box are filled with wafers, one to two inches long and one-quarter to one-half inch in width, cut from sheet zinc. Although the method has been used with apparent success at two or three small mines, it has not gained general favor.

Zinc-Dust Precipitation.

The first use of a pulverulent precipitant in conjunction with the cyanide process was the utilization of zinc-dust or zinc fume, a by-product of zinc smelting, in the operation of the Sulman and Teed bromo-cyanide process. The original proposal of introducing the dust into a cone, through which the solution flowed upward, never met with much favor, presumably on account of exposure to the air and the difficulty of preventing finely divided precipitate from overflowing with the solution at the top of the cone. The addition of zinc dust to the sump tank during air agitation of the solution, previous to the pumping of the whole mixture through a filter press, was first introduced by Mr. Chas. W. Merrill, at a Montana

plant. Although a similar form of zinc-dust precipitation was early in use at the Golden Gate Mill, Mercur, Utah, U. S. A., it remained for Mr. Merrill to make the final improvements in zinc-dust precipitation after he had introduced it at the Homestake Mine, Lead, South Dakota, U. S. A. In the original Homestake installation, a filter press having rectangular frames was employed. The zinc-dust emulsion, prepared by agitation of a weighed amount of zinc dust with a small amount of solution in a closed cone, was forced out through a rubber hose attached to the bottom of the cone and sprayed upon the surface of the solution in the sump while undergoing violent air agitation. As soon as the zinc-dust emulsion had all been introduced, the air was shut off and the whole contents of the tank pumped into the filter press.

One of the most important improvements was the elimination of agitation in contact with air, through the introduction of the zinc dust directly into the suction of the pump by means of a special belt feeder. This resulted in more efficient precipitation, as well as in considerable saving of zinc, sufficient agitation being realized by the passage of the solution through the pumps and pipe lines. As a matter of fact, a great part of the precipitation, in many cases, takes place in the filter press; and, in any event, the last of the precipitation, which is the most difficult to obtain, invariably takes place at this stage. Strangely enough, it was only after this improvement was made that the ill effect of the introduction of air with the solution during precipitation was properly appreciated. In present-day practise every precaution is taken to exclude air, so far as possible. A small air leak in the suction of a precipitation pump will invariably cause high tails. Interference of air with precipitation is due to resolution of gold and silver and, as has been pointed out by Mr. Allan J. Clark, to the formation of a superficial coating of calcium carbonate upon the zinc particles. The plate-and-distance frame type of filter press has been invariably used for zinc-dust precipitation. This type of filter press has been improved by Mr. Merrill, for use in connection with the application of pulverulent precipitants, by a special design employing triangular plates and frames. The solution is introduced at the lower apices of the triangular chambers,

thus giving thorough agitation of the contents of the chambers with the solution being precipitated.

The Merrill precipitation press, as shown in Fig. 9, is built with either 36-in. or 52-in. plates and frames. The frames are made 1½ in., 2 in. or 3 in. in thickness. The 1½-in. and 2-in. frames are generally used for precipitating gold solutions, while the 3-in. frame is used for solutions in which silver predominates. The Merrill Company estimates the precipitation capacity necessary in any particular case as follows: The number of frames used depends upon the weight of solution precipitated, the unit taken being the U. S. ton of 2000 pounds. One chamber of 2 in. x 36 in. is allowed for each 12½ tons of gold solution precipitated per 24 hours, while one chamber of 3 in. x 36 in. is allowed for each 10 tons of silver solution precipitated per 24 hours. The 52-in. chambers have just double the capacity noted for the 36-in. chambers; i. e., 25 tons for the chambers 2 in. deep upon gold solution and 20 tons for the chambers 3 in. deep upon silver solution. The amount of metal in solution determines the rate of feed of the zinc dust and the frequency of the clean-up.

Perhaps the best practise in operating the filter press is to use a double cloth, canvas next to the plate, and on top of this twill or muslin. The heavy cloths, which give the necessary strength, remain on the press until they finally fail through becoming rotten or torn. The light cloth is removed each time the press is taken down, cleaned, burned and the ashes added to the precipitate.

The solution may be pumped to the filter press by any appropriate form of pump, or, under favorable conditions, may be delivered by gravity. The geared plunger-type pump, equipped with external packing glands and either belt-driven or direct connected to an electric motor, is the most generally used type. Contrary to supposition, the wear upon the plunger due to the zinc dust and precipitate is insignificant. The centrifugal pump has been occasionally used for this purpose, and, where violent agitation is desirable, as in aluminum-dust precipitation, it might at times be preferred to the plunger type.

With the present-day continuous method of precipitation, an efficient zinc-dust feeder is of vital importance. A satisfac-

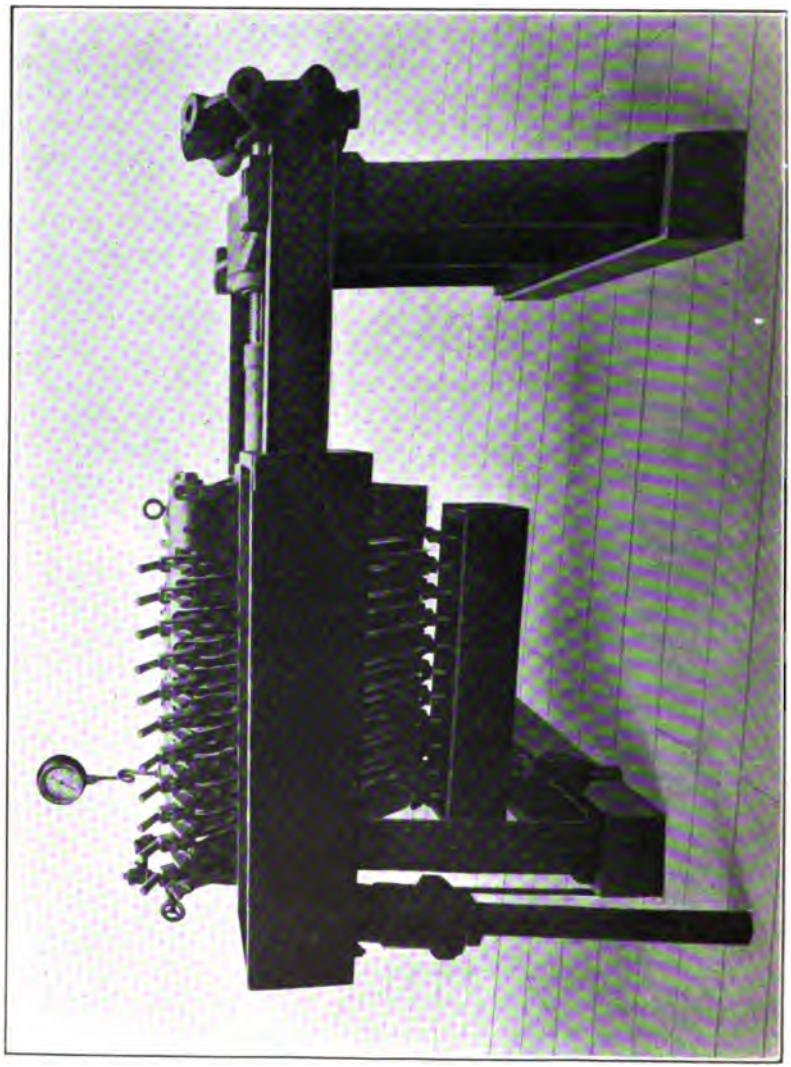
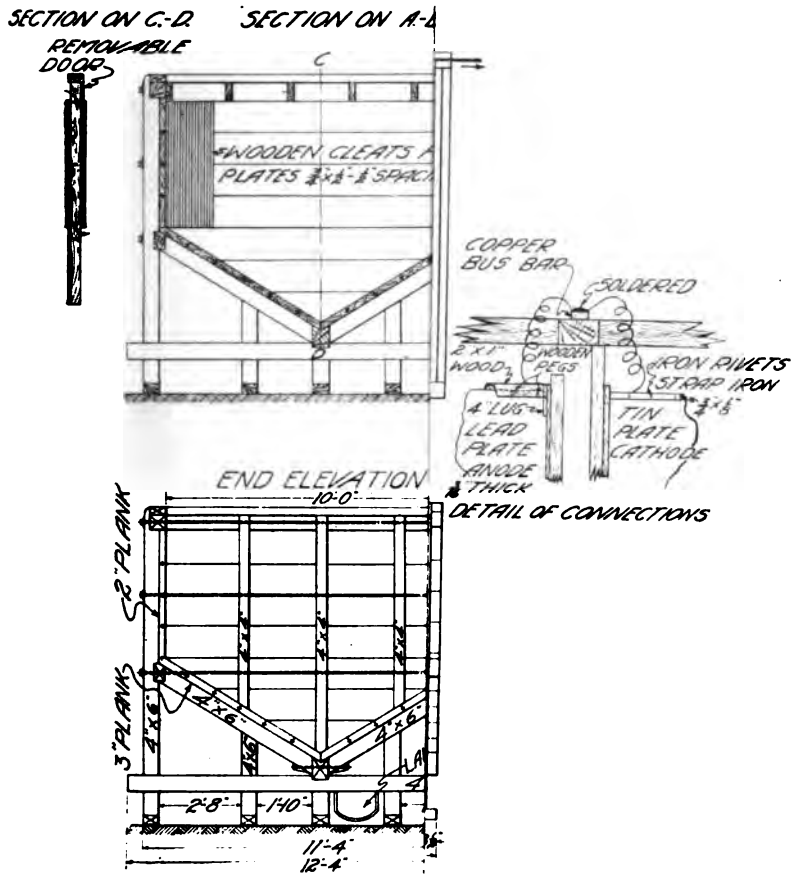


Fig. 9. Merrill Precipitation Press.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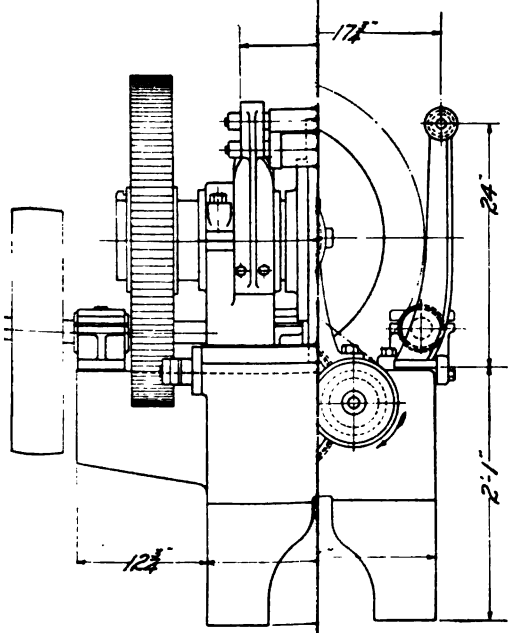
SECTION ON A.-
REMOVABLE DOOR
C
WOODEN CLEATS
PLATES
COPPER BUS BAR
SOLDERED
2" x 1" WOOD
WOODEN PEGS
IRON RIVETS
ST. FLAT IRON
4" LUG
LEAD PLATE ANODE
TIN PLATE CATHODE
THICK
DETAIL OF CONNECTIONS
END ELEVATION
10'-0"
2" PLANK
3" PLANK
4" x 6"
2" x 6"
2'-8"
1'-10"
11'-4"
12'-4"



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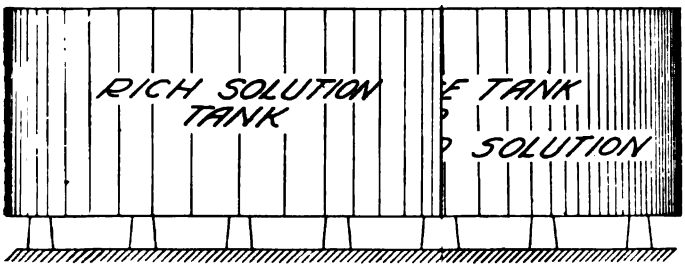

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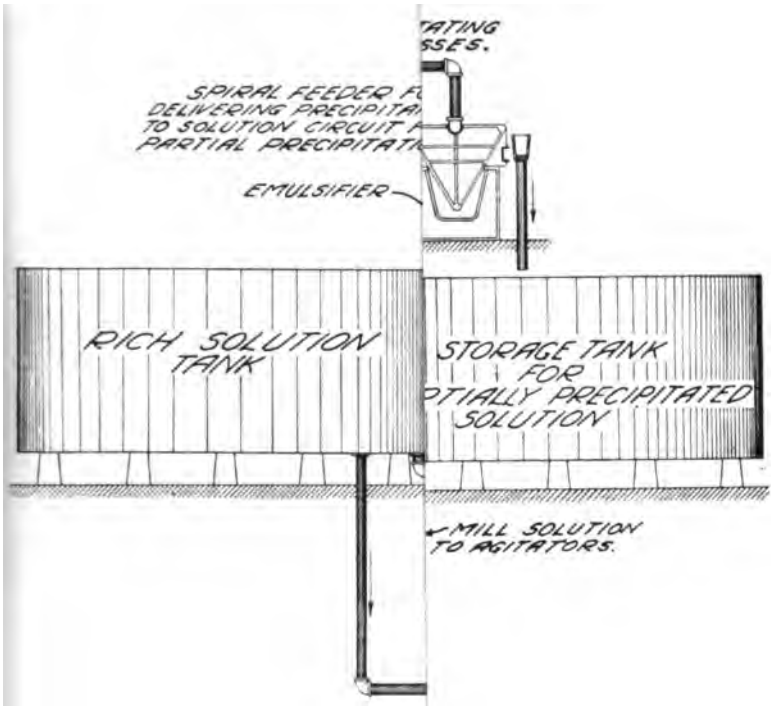
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TO AGITATORS.

tory feeder should be capable of very close adjustment and should maintain a regular rate of feed with the minimum attention. The design and construction of a satisfactory feeder is considerably more difficult than might appear at first sight. The original type as proposed by Merrill was an endless belt. On the top surface of this belt was placed the amount of zinc necessary to precipitate the given tank of solution. The belt was actuated by means of a series of floats, so as to cause the

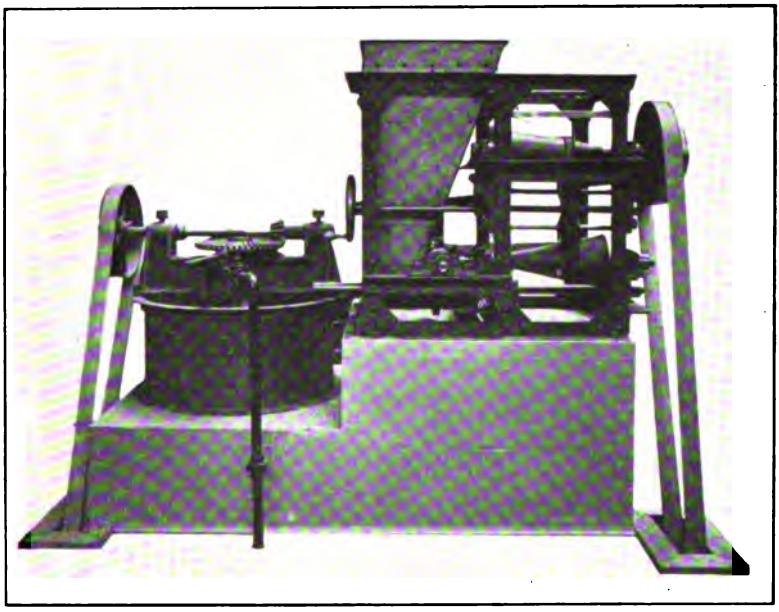

Fig. 10. Latest Type of Zinc-Dust Feeder.

belt to travel forward and feed the zinc dust in exact proportion to the rate at which the solution was lowered in the sump tanks. A later type, illustrated in Fig. 10, makes use of a screw located at the bottom of a hopper, the hopper being provided with a hammering arrangement or a reciprocating arm to prevent arching of the zinc dust. Provision for regulating the speed of the screw is made by means of double cone and belt drive. Another type of feeder makes use of a rotating drum located at the bottom of a hopper, a slide at the side determining the amount of zinc dust fed. In this type, it is also neces-

sary to make provision for jarring the hopper, so that the zinc dust will not arch over. The difficulty of "arching" is particularly noticeable during damp weather. The feeder may discharge directly into a stand pipe which communicates with the suction of the pump, or it may first meet a small jet of solution and pass through a miniature tube mill or grinding pan, which scours and brightens the particles of zinc dust.

One interesting and important development made in connection with zinc-dust precipitation has been the introduction of what are known as the partial and complete-precipitation circuits. Usually, when operating this system, two distinct sets of zinc-dust feeders, pumps, pipe lines and precipitation presses are provided. In one system a sufficient rate of feed is maintained to give barren solution, while in the other just sufficient feed is maintained to precipitate the bulk of the gold and silver. The amount of solution completely precipitated is determined by the barren solution required for the final washes. In case only one set of precipitation apparatus is available, the benefits of this system may be realized by maintaining a heavier feed of zinc dust during the time that barren solution is desired. Then the solution is diverted to a special sump tank, and the feed of zinc dust is at first entirely cut off and later increased to maintain the tail solution at the point desired.

Figure 11 shows the single-solution circuit, in which all solution is completely precipitated as ordinarily used; and Figure 12 shows the double-solution circuit, in which the solution to be precipitated is divided as described above.

Rapid qualitative tests for gold and silver in solution are of great value in connection with the operation of zinc-dust precipitation. A satisfactory method for gold is that of Dowsett, which is very generally used. A 10% solution of sodium sulphide may be used as a rough qualitative indication of the presence of silver. However, this test fails in event of there being other metals in solution which give dark-colored sulphides. The writer has previously described a rapid volumetric method for silver which gives results quite as accurate as the fire assay, but which requires about half an hour for each determination.

Inasmuch as zinc dust is a by-product of zinc smelting, there being little or no attempt made to specialize in its manufacture, it is not surprising that its composition should be variable, and herein lies one of the chief problems of zinc-dust precipitation. In all the years that zinc-dust precipitation has been used, little or no knowledge has been acquired regarding the specific effect of the various impurities which zinc dust may contain, with the possible exception of lead. It might be mentioned that zinc dust is very prone to carry a greater proportion of impurities than the spelter produced from the same ore, due to the volatility of such elements as arsenic, antimony, cadmium, etc.

Considerable work has been done looking toward the development of a laboratory method for determining the efficiency of various samples of zinc dust. However, the only method at present in general use is that suggested a number of years ago by Mr. Allan J. Clark. In this method the precipitating efficiency of a weighed portion of zinc dust is measured by means of the silver precipitated from an excess of 1% potassium-silver cyanide solution. This method has proven useful but cannot be always depended upon to indicate just what the particular lot of zinc dust will do under mill conditions.

In general, certain foreign brands of zinc dust have proven the most satisfactory. Trouble experienced with poor grades of zinc dust has been frequently attributed to the presence of zinc oxide, which, it is assumed, coats the particles of zinc dust. Microscopic examination tends to show that the zinc oxide does not, in general, exist as a definite coating upon the metallic particles, but rather as a mechanical mixture with them. However, there is evidence of some kind of a coating upon the particles. This has been attributed to a coating of carbide.

The results and costs of zinc-dust precipitation vary with the locality and the character and grade of the ore treated. The figures given below, from widely separated plants treating a variety of ores, are merely indicative of what may be expected.

The Portland Mill, at Colorado Springs, U. S. A. treating roasted telluride gold ores, employs a partial-precipitation circuit for the strong solution and a complete-precipita-

tion circuit for the weak solution. The average figures for three months during 1914 were as follows: approximately 1100 tons of strong solution, containing $3.35 per ton of 2000 lbs., were precipitated daily to a $0.25 tail, with a zinc dust consumption of 0.136 lb. per ton. Approximately 1000 tons of weak solution, containing $2.54 per ton, were precipitated to a $0.045 tail, with a zinc-dust consumption of 0.173 lb. per ton. A 100-ton per day plant in San Luis, Durango, Mexico, treating a silver-gold ore and employing a single-precipitation circuit, precipitated 1 part of fine silver and gold for each 0.95 part of zinc dust used. The ratio of silver to gold, by weight, was 55 to 1; percent of fine silver and gold in precipitate, 78.0. Total cost of precipitation and melting per fine ounce of doré bullion, 1.0c.

Another plant in Mexico, treating 500 tons of silver-gold ore daily, employing a double-precipitation circuit, precipitated approximately one half of the solution in the complete circuit to 1 or 2 cents per ton, with a zinc dust consumption of 1.1 parts for each part of fine silver and gold precipitated. The other half of the solution was precipitated in the partial circuit to a 10-cent tail, with a zinc dust consumption of 0.74 part for each part of fine silver and gold precipitated. The ratio of silver to gold by weight was 150 to 1. Percent of fine silver and gold in precipitate, 78. Total cost of precipitation and melting per fine ounce of doré bullion 0.913 cents.

The Homestake plants, Lead, South Dakota, U. S. A., treating a low-grade gold ore, show the following results, covering a period of one month:

Plant	Heads	Tails	Pounds zinc dust per ton of solution	Cost of precipitation per ton of ore treated
No. 1 sand	$2.94	$0.018	0.173	$0.0123
No. 2 sand	2.77	0.034	0.174	0.0109
Slime	1.19	0.028	0.160	0.0165
Average on whole ore	1.87	0.026	0.165	

The percentage of gold in the precipitate averages 9.50 and the silver 3.34, as taken from the press. After acid treatment, the gold is 16.55% and the silver 5.83%.

Comparative costs of zinc-dust and zinc-shaving precipitation show considerable advantage in favor of zinc dust.

At the Homestake, when using zinc-shaving precipitation for waste solution, the cost per dollar recovered was $0.1608, while with the zinc dust the cost was $0.0449. The comparison of two plants in the El Oro District gives the cost of zinc-dust precipitation, at one, as $0.079 per ton of ore treated, while the cost of zinc-shaving precipitation, at the other, is $0.201 per ton of ore treated. The relationship between the cost of the two methods of precipitation depends, to a considerable extent, upon the relative cost of zinc dust and sheet zinc; thus, when zinc dust is high and sheet zinc is low, the differences may not be so great.

Zinc-dust precipitation is rapidly gaining in favor. The reasons for this are that a minimum amount of labor is required for its operation; there is a minimum loss in handling both zinc and precipitate, and, furthermore, the precipitate is more effectively protected from theft than is the case with zinc shavings. It also seems to be somewhat better able to cope with solutions containing copper. This is probably on account of the fact that fresh precipitant is constantly being added.

Closely related to zinc dust precipitation is the possibility of using other pulverulent precipitants with similar equipment. Precipitation with powdered aluminum is mentioned elsewhere. A possibility which Mr. Chas. W. Merrill has long had in mind is the use of various brittle alloys so compounded as to give the desired qualities for precipitation, as well as possessing the necessary brittleness so that they may be finely ground into a dust or powder. At first sight, it might appear that there would be a number of such combinations possible. However, careful investigation has led to the belief that this is a very desirable, but perhaps rather restricted, field.

REFINING.

The early practise of selling the precipitate to smelters is still adhered to by a few companies, but the majority convert into bullion before marketing. Cyanide bullion varies greatly in fineness, depending upon the character of the ore treated as

well as the equipment provided for refining and the degree of skill exercised in its use. It is, obviously, not good practise to carry local refining to the point where the cost is greater than the advantages to be realized from marketing higher-grade bullion. The only case that I know of where fine bullion is produced which requires no further refining is that of the Nipissing Mining Company, Cobalt, Ontario, Canada. Here, unusual conditions make the production of fine bullion a comparatively easy matter.

Preliminary acid treatment of the precipitate has been found unnecessary in most cases where silver predominates, but is still adhered to in the majority of cases for gold precipitate.

The oil-fired tilting-crucible melting furnace has now largely replaced the earlier types of stationary-crucible furnaces, thus making the melting operation much less laborious, as well as considerably reducing its cost.

The Tavener method of refining, involving the melting of the precipitate in a small reverberatory furnace with various fluxes and lead, followed by cupellation, is still in general use in South Africa, but has not gained ground in this country.

The Homestake method of refining, involving acid treatment and briquetting with lead flux, followed by melting and cupellation in the ordinary English cupel furnace, as well as the treating of all the by-products in a small blast furnace, is used by a few American plants.

The melting of the precipitate, briquetted with the proper fluxes, in a small blast furnace, followed by cupellation of the lead, has been found of advantage when dealing with a large volume of low-grade gold precipitate. Losses from dusting, which might appear to be the chief objection to this method of melting, are claimed to be insignificant when a proper flux system is provided. This method of melting is more economical than either the Tavener or Homestake practice.

The electric furnace has also been used in a few cases.

The most simple and satisfactory method of converting the high-grade precipitate which is obtained, by proper manipulation, from ores in which silver predominates is to melt the precipitate directly, with the minimum proportion of flux, in the

tilting type of furnace. A few mills use a double-chamber tilting furnace, in which the flame comes in direct contact with the charge being melted. This furnace is perhaps more economical of fuel, but, unless the precipitate is briquetted, there is greater risk of loss through dusting than when the precipitate is melted in a closed crucible. In the case of silver precipitate, with proper manipulation in the crucible furnace, it is a serious question whether it pays to briquette, the losses being less under these conditions than the cost of briquetting.

Assuming that only perfectly clear solution is precipitated, which eliminates all matter in suspension which would tend to lower the grade of the precipitate, much can be accomplished in raising the proportion of gold and silver in the precipitate by the judicious use of pregnant solution. Fig. 13 shows a general scheme of refining used by the writer in connection with zinc-box precipitation some eight years ago. The novel feature is the washing of the fine precipitate from the zinc box with pregnant solution into the filter press, where it is collected. The pumping of pregnant solution through the filter press is continued at intervals, until the tail solution rises to approximately the value of the pregnant solution precipitated. During the earlier stages of pumping, the tail solution from the filter press was of low enough grade to divert to the milling solution, but, during the later stages, it was advisable to return it to the head of the zinc boxes. With solutions in which silver occurred in the ratio of 50 parts to 1 part of gold, precipitate was at times obtained which contained approximately 90% of silver and gold. There was no difficulty in obtaining precipitate, regularly, well over 80% of silver and gold. Precipitate of this grade is very easily melted, with a minimum consumption of fluxes and fuel, and, of course, produces a high-grade bullion. Later, at a certain Mexican plant, where this plan was adopted upon my suggestion, the grade of the precipitate was very materially raised and the fineness of the bullion was increased from 800 to 900. This resulted in a monetary saving of several hundred dollars per month. A similar plan appears to be feasible with zinc-dust precipitation. It is still a question as to how far such a plan could be carried with solutions in which gold predominates.

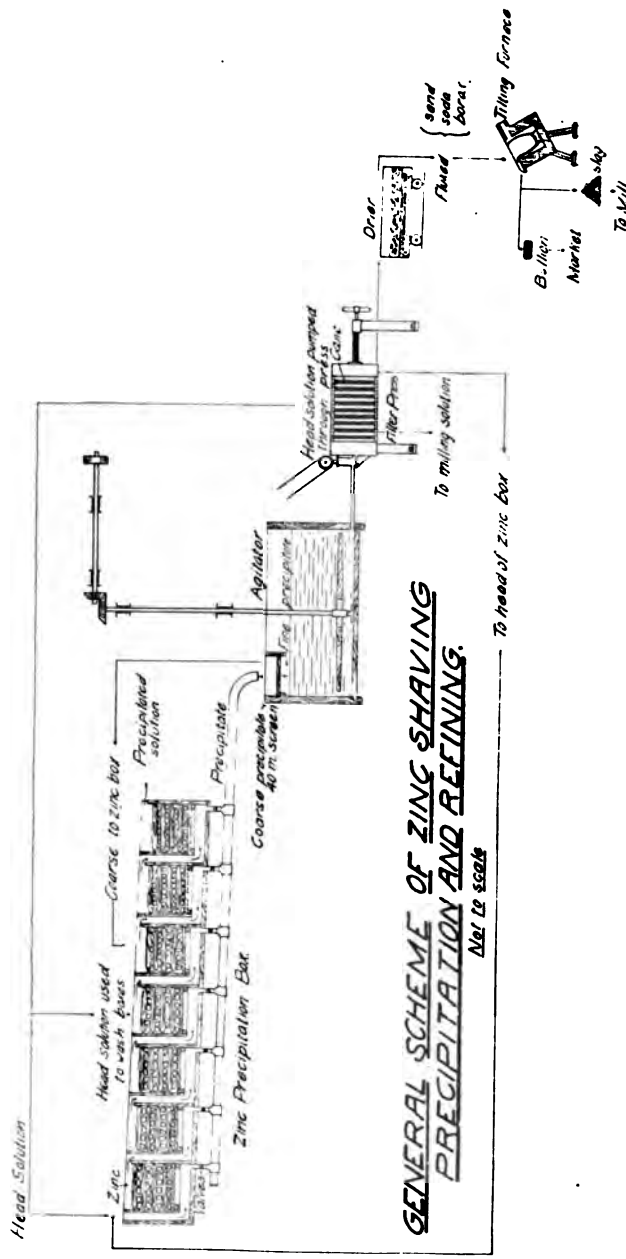
GENERAL SCHEME OF ZINC SHAVING PRECIPITATION AND REFINING.
Not to scale
Head Solution
Zinc
Head solution used to wash fines
Zinc Precipitation Box
Coarse to zinc box
Precipitated solution
Precipitate
Coarse precipitate 40 m. screen
Agitator
Fine precipitate
Head solution pumped through press cloths
Filter Press
To milling solution
To head of zinc box
Dryer
Sand
Soda
Borax
Tilting furnace
Bullion
Market
Slag
To Mill

Fig. 13.

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"A Development in Electrolytic Precipitation of Gold and Silver from Cyanide Solutions", E. M. Hamilton. Proceedings of the Chem. Met. and Min. Soc., S. A., Vol. 4, pp. 342-359. (A very good article on the practice at Minas Prietas.)

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"Electrolytic Precipitation of Cyanide Solutions", C. P. Richmond. E. and M. J., Vol. 83, pp. 512-515. (A very good account of the San Sebastian, Salvador, practice.)

"Electrolytic Precipitation from Potassium Cyanide Solution", J. H. Jory. E. and M. J., Vol. 71, p. 779. (Discussion of the Siemens-Halske Process.)

"The Electrical Precipitation of Gold on Amalgamated Copper Plates", T. K. Rose. I. M. and M., Vol. 8, pp. 369-375. Discussion, Vol. 8, pp. 375-378. (Deals only with subject indicated by title.)

Charcoal Precipitation.

"On Charcoal Precipitation from Auro-Cyanide Solutions", John I. Lowles. I. M. and M., Vol. 7, pp. 190-196. Discussion, Vol. 7, pp. 196-198. (Describes the practice as formerly carried on in the Victoria district of Australia.)

"Solution and Precipitation of Cyanide of Gold", S. B. Christy. A. I. M. E., Vol. 26, p. 749. (Refers to Johnson's patent and gives an account of laboratory experiments with charcoal precipitation.)

"Precipitating Action of Carbon in Cyanide Solutions", O. C. Ralston. Min. Sci. Press, Vol. III, pp. 77-78. (General discussion of the phenomenon of precipitation of gold from cyanide solutions by carbon.)

Aluminum Precipitation.

"Aluminum Precipitation at Deloro, Ontario", S. F. Kirkpatrick. E. and M. J., Vol. 95, pp. 1277-1278. (An account, by the inventor, of the first installation for aluminum dust precipitation, together with additional information on the subject.)

"Aluminum Precipitation at Nipissing", E. M. Hamilton. E. and M. J., Vol. 95, pp. 935-939. (Gives a historical review of the subject and an account of the practice at the Nipissing mill, calling particular attention to the interference of arsenic in the presence of zinc.)

"The Mill and Metallurgical Practice of the Nipissing Mining Company, Ltd., Cobalt, Ontario, Canada", G. H. Clevenger. July, 1914, Bulletin A. I. M. E., pp. 1486-1496. (Discussion of aluminum precipitation as practiced at the Nipissing mine, together with its possible application elsewhere.)

"Aluminum Precipitation at Nipissing", E. M. Hamilton. E. and M. J., Vol. 99, pp. 568-571. (General discussion of aluminum precipitation.)

"Aluminum Precipitation", G. H. Clevenger. To be published shortly in the E. and M. J. (Continuation of the discussion contained in the two above articles.)

Zinc Precipitation.

"Solution and Precipitation of Cyanide of Gold", S. B. Christy. A. I. M. E., Vol. 26, pp. 759-766. (An early discussion of zinc-shaving precipitation.)

"The Precipitation of Gold from Cyanide Solutions", W. A. Caldecott and E. H. Johnson. Proceedings of the Chem. Met. and Min. Soc., S. A., Vol. 4, pp. 263-272. (Deals largely with the theory of zinc-shaving precipitation.)

"Consumption of Zinc on Cyanide Plants—Nature, Cause and Effect", Walter H. Virgoe. Proceedings Chem. Met. and Min. Soc., S. A., Vol. 4, pp. 615-638. (Deals with zinc-shaving precipitation.)

"Cyanide Practice", Alfred James. I. M. and M., Vol. 3, pp. 399-403. (Deals largely with the theory and chemistry of zinc-shaving precipitation.)

"Precipitation", E. H. Johnson. From "A Text-Book of Rand Metallurgical Practice", Vol. 1, pp. 245-254. (Account of zinc-shaving precipitation practice on the Rand.)

"Cyanide Precipitation and Clean-up at the Portland Mill", J. M. Tippett. Western Chemist and Metallurgist, Vol. 4, pp. 17-20. (Account of precipitation of low-grade gold solutions. Particular mention is made of the formation of white precipitate and its effect upon lowering the grade of the precipitate.)

"An Investigation of Zinc-Box White Precipitate", Roy F. Coolidge. West. Chem. and Met., Vol. 5, pp. 281-289. (Title indicates the contents of this paper.)

"Short Zinc", Articles by F. L. Bosqui, W. T. Willis, Bertram Hunt and R. Stuart Browne, from "More Recent Cyanide Practise", pp. 273-278. (Discusses the cause and effect of short zinc.)

"Screen Trays for Zinc Boxes", E. and M. J., Vol. 88, p. 990. (Detail of trays used with zinc-boxes for treating short zinc.)

"A New Method of Precipitation by Zinc", John S. MacArthur. Journal Chem. Met. and Min. Soc., S. A., Vol. 13, pp. 310-311. (Describes a new method of precipitation employing zinc wafers.)

"The Sulman-Teed (Bromo-Cyanide) Process of Gold Extraction", H. Livingstone Sulman and Frank L. Teed. Journal Soc. Chem. Ind., Vol. 16, pp. 965-966. (An account of the first use of zinc-dust precipitation.)

"The Metallurgy of the Homestake Ore", C. W. Merrill, A. I. M. E., Vol. 34, pp. 594-595. (Early account of Homestake precipitation practise.)

"Zinc Dust Precipitation", C. W. Merrill. E. and M. J., Vol. 92, p. 407. (Early account of Homestake zinc-dust practise.)

"Zinc Dust Precipitation by the 'Merrill' Process", F. Wartenweiler. From "A Text-Book of Rand Metallurgical Practise", Vol. 2, pp. 270-276. (Describes zinc-dust precipitation as practised on the Rand.)

"The Metallurgy of the Homestake Ore", Allan J. Clark and W. J. Sharwood. I. M. and M., Vol. 22, pp. 126-132. (A very good description of present Homestake precipitation practise.)

"Operation of the Goldfield Consolidated Mill", J. W. Hutchinson, Min. and Sci. Press, Vol. 102, p. 716. (A very good account of zinc-dust precipitation as practised at this mill.)

"The Refining of the Precipitate Obtained by means of Zinc in the Cyanide Process of Gold and Silver Extraction", G. H. Clevenger. A. I. M. E., Vol. 34, pp. 891-897. (Discusses the nature of zinc-shaving and zinc-dust precipitate.)

"Zinc-Dust", "The Metallurgy of Zinc and Cadmium", Walter Renton Ingalls. "Composition", pp. 528-530. "Formation", pp. 521-522. "Preparation for Market", pp. 526, 666.

"Zinc Dust Tests", W. J. Sharwood, Journal Chem. Met. and Min. Soc., S. A., Vol. 12, pp. 332-338. (Discusses the nature of zinc dust and gives tests for its valuation.)

Miscellaneous Proposed Methods of Precipitation.

"The Solution and Precipitation of the Cyanide of Gold", S. B. Christy. A. I. M. E., Vol. 26, pp. 746-771.

"Cyaniding Gold and Silver Ores", H. Forbes Julian and Edgar Smart. Second Edition, pp. 160-166.

Refining.

"Treatment of Cyanide Precipitate", Herbert A. Megraw. E. and M. J., Vol. 97, pp. 505-509; 606-612. (Gives an account of various modern methods of refining and melting.)

"The Refining of the Precipitates obtained by means of Zinc in the Cyanide Process of Gold and Silver Extraction", G. H. Clevenger. Trans. A. I. M. E., Vol. 34, pp. 891-917. (Describes methods of refining as practised some time ago.)

"Operation of the Goldfield Consolidated Mill", J. W. Hutchinson. Min. and Sci. Press, Vol. 102, pp. 716-719. (An account of refining by smelting in the lead blast furnace.)

"The Metallurgy of the Homestake Ore", Allan J. Clark and W. J. Sharwood. I. M. and M., Vol. 22, pp. 132-154. (An account of Homestake method of refining.)

"Smelting", "A Text-Book of Rand Metallurgical Practice", E. H. Johnson. Vol. 1, pp. 266-285.

"The Smelting and Refining Plant", "A Text-Book of Rand Metallurgical Practice", Vol. 2, pp. 280-286. (Describes Rand refining practice.)

"Electric Furnace at Lluvia de Oro", H. R. Conklin. E. & M. J., Vol. 93. pp. 1189-1192. (Describes an electric furnace for melting precipitate, also gives details of the operation.)

"Electric Furnace for Gold Refining at the Alaska-Treadwell Cyanide Plant", W. P. Lass. Bulletin A. I. M. E., July 1915, pp. 1443-1447. (Describes a simple electric furnace used for treating high slags resulting from the melting of cyanide precipitate.)

DISCUSSION

Mr. Clennell.

Mr. J. E. Clennell stated that a comparative run had been recently made between zinc precipitation and aluminum precipitation at the Butters' Divisadero Mine, Salvador, C. A., in which advantage regarding cyanide consumption was shown by aluminum precipitation.

Prof. G. H. Clevenger,* Mem. Am. Inst. M. E., stated that the paper giving an account of this work had been published since he wrote the paper under discussion. He, however, stated that he was not prepared to admit the full saving in cyanide which is claimed by those making the tests at Divisadero, as, in the first place, the comparison is made against poor zinc-shaving precipitation practice, as evidenced by certain of the results of zinc-shaving precipitation recently obtained in the Tonopah district, and, further, that there was about one-half pound of cyanide which had been credited to aluminum precipitation which the experimenters did not seem to be able to account for. Prof. Clevenger then asked Mr. Chas. Butters if, when they began aluminum precipitation, they threw away all of the old cyanide solution containing zinc. Prof. Clevenger.

Mr. Butters replied that they had not thrown away any solution. Mr. Butters.

Prof. Clevenger then stated that those in charge of the experiments at Divisadero had searched for everything else possible in solution which would account for this extra saving of one-half pound of cyanide and that they had considered everything, with the exception of the most probable constituent, i. e., the zinc; in other words, that during the first three months of operation with aluminum precipitation, cyanide would be regenerated from zinc potassium cyanide remaining in solution, so that there would be a constant gain in cyanide. He added that they were getting more cyanide than was coming to them, and that later, when this had disappeared from the solution, the cyanide consumption would increase. Prof. Clevenger.

Mr. Chas. Butters,** Mem. Am. Inst. M. E., stated that, in connection with this test, he had instructed his staff that the only thing that would convince him of there being less cyanide used would be when he was buying less. He further thought that the effect of the zinc would largely disappear in three months. Mr. Butters.

Prof. Clevenger then stated that, on this account, he was more interested in the results for the next three months than in those which had just been quoted. Prof. Clevenger.

Mr. Butters said that it was impossible at the present time to give these figures, but that he hoped to be able to do so later. On the whole, he felt that there was a certain saving in the cost of precipitation when aluminum was used. Mr. Butters.

Prof. E. A. Hersam,† Mem. Am. Inst. M. E., stated that he should like to secure some data regarding the solvent action of double cyanide of potassium and zinc upon gold and silver. A good deal had been surmised in this connection, but what he wished was some actual figures. Prof. Hersam.

Mr. C. W. Merrill, Mem. Am. Inst. M. E., stated that Mr. Sharwood had gone into this matter very thoroughly. Mr. Merrill.

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Prof. Clevenger. **Prof. Clevenger** added that Mr. Sharwood's paper could be found in the Journal of the American Chemical Society, Vol. 25, p. 580.

Mr. Simonds. **Mr. E. H. Simonds,**† Mem. Am. Inst. M. E., said that, particularly in view of the high prices of the metals, the subject of precipitation is of especial interest at this time, for any improvements which could be made would mean a considerable saving. He also said that he had found that a solution containing 0.015% of cyanide could be as effectively precipitated as one containing a quarter of a pound, but that after the zinc shavings had been used 48 hours, they became coated. Therefore, other methods of precipitation were tried, including aluminum dust, but the results in general were no better than those previously obtained with zinc. He also said that he thought that weak solutions could be precipitated with zinc, provided they were clean.

Prof. Hersam. **Prof. Hersam** said that he wished to call attention to the work which the late Professor Samuel B. Christy had done upon electrolytic precipitation. The paper, which was complete at the time of Professor Christy's death, goes into the whole subject very thoroughly. He added that Professor Christy felt that, in its fundamentals, electrolytic precipitation had the advantage over any other form of precipitation.

Mr. Butters. **Mr. Butters** said that he had spent half a million dollars upon electrolytic precipitation and in the end had been beaten by zinc precipitation, but still he was hopeful that electrolytic precipitation might eventually be brought to a successful issue.

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Paper No. 189

THE SMELTING AND REFINING OF LEAD.

By

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The starting-point of a review of the present state of smelting of lead ored in the United States is the introduction of blast-roasting which has revolutionized the details of practice not only here, but in all lead-producing countries. Thus the reverberatory furnace has become obsolete the world over for the smelting of high-grade galena concentrates. The ore-hearth, on the other hand, has maintained its important place in the treatment of the non-argentiferous ores of the Mississippi Valley.

Many theories have been proposed to explain the phenomena taking place in blast-roasting; most of them have been abandoned; the statement by Richter that blast-roasting is nothing more or less than an enforced ordinary oxidizing roast accompanied by sintering, meets all practical wants. The presence of lime in a charge, at first deemed essential, has been proved to be not absolutely necessary. This does not preclude that lime forms a valuable flux with lead ores, which is not the case with copper-bearing materials. Some exothermic reactions take place with lead ores, as shown by Percy, Hutchings and Bannister, which have not been noticed with other sulphide materials.

In the practice of blast-roasting the composition of the charge is of first importance; and here the calorific value, the ultimate analysis and the physical make-up have to be considered. The heat generated by oxidation has to be sufficient for agglomeration and not in any great excess over the amount required. The two rival processes in the United States, the

Huntington-Heberlein and the Dwight-Lloyd, diminish the calorific power of their charges by a rough-roast which reduces the sulphur content to as low a figure as 10 or 11 per cent, but usually holds it between 15 and 18 per cent. The great range of 10 and 18 per cent is due to the other components of the charge; thus the lead content varies from 10 to 50 per cent, while the percentage of silica is held within narrower limits, averaging 12-15 per cent. The size of the charge-particles varies from slime concentrate to ½ in.; ores are usually not finer than 4-mesh, fluxes are preferably coarser than sulphide minerals. A recent comparison of the work of the two rival apparatus at Murray, Utah, and East Helena, Mont., has brought out the following:

Item	At Murray Advantage lies in favor of	At East Helena Advantage lies in favor of
Cost of installation	D. & L.	D. & L.
Cost of roasting	H. & H.	Even
Adaptability to charge	D. & L.	D. & L.
Metal Loss	Even	Even
Physical condition of product	H. & H.	D. & L.

The use of blast-roasted materials in the blast-furnace instead of the products of the hand or mechanical reverberatory-roasters has greatly increased the smelting power and has changed to some extent the lines of the furnace and the mode of operating. A. S. Dwight has recently given some interesting data relating to a furnace 48 by 162 in. at the tuyère-section which show for 24 hours the following tonnages: 180 Brückner product, 200 Huntington-Heberlein, 227 Huntington and Heberlein with fines largely removed, 285 Dwight-Lloyd with fines largely removed. In smelting raw or roasted ores, it has been essential for the sake of a good reduction to have the charge descend somewhat slowly in the furnace; this necessitated an angle of bosh of the side-jackets of about 20 degrees and a flare of the brick shaft above of 1 inch in 1 foot. With a blast-roasted charge, it has been found that a bosh with an angle of 10 degrees and vertical side-walls did better work, in that it gave a better slag, extracted a higher percentage of lead, and burnt off more sulphur. L. D. Anderson, governed by the work at Midvale, Utah, suggests a contraction of the throat area, which would make the profile of the lead furnace

resemble that of the iron blast-furnace. The use of the blast-roasted ore has resulted in a reduction in the blast-pressure, the formation of slags of higher silica content, and the use of a lower percentage of coke than was customary a few years ago. Of course, the reduction of the amount of fines in the charge has greatly reduced the formation of flue dust, and thus simplified the apparatus for the collection of this intermediary product. With the majority of blast-furnaces, the lead is mainly the carrier of precious metals; therefore the lead content of the charge is low, say 15 per cent. Thus a blast-furnace of the United States Smelting and Refining Co., at Midvale, Utah, 45 by 160 in. at the tuyère-section with ten 3.5-inch tuyères to a side and a working height of 17 ft., treats in 24 hours 200 tons charge with 13-15 per cent lead. In the two smelteries of East Helena, Mont., and Herculaneum, Mo., the practice resembles more the work of European plants, as the lead ore is a galena concentrate which is smelted with siliceous material, and furnishes charges running as high as 40 per cent lead. Thus at East Helena a blast-furnace 48 by 136 inches at the tuyère-section with 16 tuyères 3.5 in. in diameter and a working height of 18 ft., treats in 24 hours 270 tons charge with 30-40 per cent lead; at Herculaneum a furnace 42 by 192 inches at the tuyère-section with 12 tuyères 4-4.5 in. in diameter and a working height of 17 ft., treats in 24 hours 225 tons charge with 40 per cent lead.

Lead bullion is desilverized by the Parkes process, if we except the refineries at Grasselli, Ind., and Trail, B. C., which have in operation the Betts electrolytic process. An important innovation with the Parkes process is supplementary treatment at Omaha, Neb., and East Chicago, Ind., of the refined lead by the Pattinson process in order to obtain from bismuth-bearing lead bullion, as market product, corroding lead with less than 0.05 per cent bismuth. At Omaha, metallic bismuth is produced; the bismuth content of lead bullion treated at East Chicago is not sufficiently high to warrant going so far. The research of Junge has shown that lead with 0.2 per cent bismuth is not attacked by sulphuric acid of 60 degrees B. at the temperature of the sulphuric acid chamber. The new works of East Chicago have a monthly capacity of 50,000 tons lead bul-

lion when running 25 days; having been only recently constructed, they show modern ways of handling materials. The electrolytic plant at Grasselli also produces metallic bismuth and hard lead; that of Trail does not extract bismuth or antimony from the anode mud.

The treatment of blast-furnace matte has undergone some radical changes. Formerly this intermediary product was thoroughly roasted in different kinds of reverberatory furnaces, and added to the blast-furnace charges until its copper content had been enriched to about 14 per cent. The smelting of this pulverulent roasted product caused much trouble, as it separated from the siliceous part of the charge and disturbed the work of the furnace. All this has been obviated by rough-roasting the matte and then blast-roasting it either with siliceous ores or with the other ores that are to be used for making up the blast-furnace charge. The further treatment of 14 per cent copper matte is now carried on in basic converters. The older method, worked out at Maurer, N. J., is to treat lead-copper-iron matte in the same manner as copper-iron matte, i. e., with the additions of siliceous ores. A charge of matte and ore is blown until the ore has been scorified, the slag is poured off, and a second charge of matte followed by ore is given and blown; the operations are continued until the copper in the matte has been brought forward to furnish white metal, which is now blown to blister copper. A departure from this standard method of treatment has been made at the smeltery of the International Smelting Co., Tooele, Utah. Here the lead-copper-iron matte is blown without the addition of siliceous ore until practically all the lead and zinc have been volatilized to be collected in a baghouse. During the blow the iron is oxidized and a large part of the copper; the mixture is transferred to a basic copper-iron matte-converter working in the usual way with siliceous ore, the oxidized iron is scorified and the oxidized copper sulphurized. The result is that the lead blast-furnace has to treat only the lead fume of the baghouse instead of a large amount of lead-iron slag. The results of the modification have been most satisfactory.

Very little speiss is produced in blast-furnaces treating ores; some refineries, especially if they are unfortunate enough.

at least from a metallurgical point of view, to have to treat arsenical silver ore from Cobalt, Ont., can not help but make speiss. There is no well established method of treating the unwelcome intermediary product. Blast-roasting has been successful in an experimental way; converting alone in a basic vessel has been a failure; converting with copper-iron matte a success.

The amount of flue dust formed in blast-furnace work has been greatly reduced. In spite of this, competition and the complaints of agricultural and other interests surrounding smelteries have forced these to make every endeavor to prevent fume and dust from passing off into the open. Thus most lead plants of any size are provided with baghouses, even when the pecuniary return they furnish is smaller than the outgo for cost, maintenance and operation. Much attention has been given to the filtration of fumes and dust. It has called attention to the important relation existing between the assay values of filtered fume and dust and the lead-silver content of matte and slag. In earlier times low values in matte and slag formed the criterion of good work; the baghouse has shown that very low assays of matte and slag are usually accompanied by high values of fume and dust; over-reduction caused volatilization. At present a balance is kept between the two.

The Cottrell system of electric precipitation of fume has been installed at Garfield, Utah, for the collection of lead-bearing fume of copper-iron matte converters after it had been carefully tested on a working scale with a single unit. Experiments with blast-roaster and blast-furnace gases have given results which show a satisfactory clearance of the gases from finely divided materials. At Trail, B. C., electric condensation is in operation.

DISCUSSION

Mr. E. B. Braden,** Mem. Am. Inst. M. E., stated that the tendency in lead smelting was to use a higher shaft, 18 ft. to 19 ft. He also said that, through the introduction of the Dwight & Lloyd sintering machine, the percentage of flue dust at the Selby Smelter had been reduced from 9% to less than 4%. Mr. Braden.

Prof. E. A. Hersam,* Mem. Am. Inst. M. E. (by letter), said that in reviewing Professor Hofman's paper, we are looking back upon Prof. Hersam.

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Prof. Hersam.

twenty-five years of progress in the lead industry. It is a period that should be rich in suggestions to us, for during these years many practices in metallurgy have come into existence and have grown to be great factors in metal production. In this time the lead processes have remained relatively little changed in principle. The new discoveries in science have seemed to have less bearing upon lead than upon many of the modern industries. Improved lighting, improved communication, improved appliances for handling, elevating, weighing, measuring and recording, and the use of oil as fuel, are the improvements, not alone in lead, but of general industry.

The absence of radical change is to be expected of an industry that has been so long established as has that of lead. The methods are tolerably fixed, and the practices appear to be near the limit of the possibilities that nature offers. Those who have most to do with current practice find least for objection in it.

The steady advance that comes when understanding is close upon the heels of practice, however, has not always been well marked in the case of lead. The patient years of slag-roasting, followed by the somewhat abrupt adoption of lime-roasting, and the late developments in mechanical sintering, reveal that we were long in discovering and adopting these newer and better methods, which involved only principles that were well known many years before. The irregular progress reflects back unfavorably upon the earlier state that existed before the improvements were made. We sometimes forget that the present time soon becomes the past, and that the last word on methods of treatment is never at any one time spoken.

Recent years have brought us, not only remarkable industrial changes which every industry must meet, but discoveries in fundamental truths to affect the understanding of things. Our lead industry will require more of metallurgists in the coming years than it has done before. There is need that the men in practice hold close to the scientific basis of ideas, not relying too much upon present practice as expressing possibilities and principles. Improvements will not be made by men who do not see the need, and can not be made by those who see only the need. Men who have only principles to apply, moreover, contribute but little to the great work that progressive industry requires to be done. The future metallurgical and economic developments in the industry, that there will need to be in the years to come, will originate from men who are grounded in underlying principles as a matter of course, and who are engaged in successful practice.

Our colleges must see to it that the men acquiring these principles at the present time, for a life devoted to practice, are not trained in habits and methods to be useful merely in the first few months of service, but rather in the disciplinary and fundamental matters that apply in all scientific understanding. A wide interest in lead, also, is in the direction of progress; and a more common discussion of whatever there is that is true is more than ever desirable to everyone concerned in our American practice.

Paper No. 180

SYMPOSIUM ON THE METALLURGY OF ZINC.

Edited by

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SOME MAIN POINTS IN THE ECONOMICS OF THE METALLURGY OF ZINC.

By

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Even before the war began, the zinc industry of the world was experiencing radical changes. The effect of the war will be to produce more changes, whereof no man can yet clearly foresee the nature and scope. Looking backward, we can now perceive that 1896, when the Wilfley table was introduced, was an historic date in the metallurgy of zinc. Making possible an improved concentration of mixed ores requiring fine grinding, the first step in the solution of the long-baffling mixed ore problem had been taken and the smelters were offered a new and bountiful supply of lead-bearing zinc ore, often high in iron, to which they had to adjust their metallurgy. Another important step in the separation of mixed ores occurred subsequently with the introduction of Wetherill's system of magnetic separation and Blake's system of electrostatic separation, but the climax occurred with the successful introduction of the flotation process at Broken Hill.

The development at Broken Hill had at least three great consequences, viz., it standardized smelting practice in Belgium and Germany; it compelled nearly all of the smelters of those countries to go on a zinc-lead basis; it showed that mixed ores

could be profitably treated, and caused a search for them to be made in all parts of the world, which within a few years resulted in the development of such mines as the Butte and Superior, of Butte, Mont., the Bawdwin, of Burma, and the Riddersk, of Siberia, to mention only three of the first order.

Let me be more explicit respecting the above statements. The total zinc production of the world, in 1913, was about 1,000,000 metric tons, of which Belgium, Holland and Germany produced about 500,000 tons. Broken Hill, in 1910-12, produced an average of 450,000 tons of blende concentrate per annum, averaging 46 to 47% zinc, which may be roughly calculated as equivalent to a yield of 170,000 tons of spelter, or about 35% of the total of Germany and the low countries.

The immense Australian ore supply was contracted to the three great German metal merchandizing firms, which distributed the ore among the smelters of Germany and Belgium. Those smelters coming thus into possession of so large, so uniform, and so regular a supply of ore, the like of which in none of those respects had ever previously been experienced in the zinc industry, were able to standardize their smelting practice, not only as to a single works but also as to many works, which was metallurgically beneficial.

The Broken Hill zinc ore was rather high in lead. In previous times, zinc smelters generally were averse to smelting ore containing more than 2 or 3% of lead, although there were a few smelters who made a practice of treating ores relatively high in lead and recovering a considerable proportion of the lead therefrom. With the advent of the Broken Hill ore, the recovery of lead as a by-product in zinc smelting became the regular thing; and in fact, the smelters of Belgium and Germany went practically upon a zinc-lead basis and even became insistent upon having a percentage of lead present in their ore, that was far above what in earlier years had been regarded as permissible.

Another radical change in the zinc industry, that was in progress previous to the war, involved the establishment of new loci of zinc smelting and was rather directly connected with the Australian development. The art of zinc smelting is one of a multiplicity of details in which the part played by many workmen spells the difference between success and failure. No

matter how careful the plans of the engineer may be, they are likely to come to naught unless there be good workmen to carry them out; and the making of good workmen requires long training. The possession of a class of workmen which has been engaged in zinc smelting during several generations is one reason why Belgium continued to be a great zinc smelting country long after its own resources were exhausted. And because of the absence of such a class of smelters, it has been universally the experience that the inauguration of new zinc smelting enterprises in new regions has been attended by difficulties which generally have wrecked the adventurer. With the advent of the great Australian ore-producing interests, however, there entered into the zinc industry a group of concerns with financial resources that enabled them to build zinc smelting works in any logical location, and with equanimity to carry them through the period in which the native population had to be taught how to smelt zinc ore. Thus, we have already witnessed the erection and operation of two zinc smelteries in Australia; we have seen the foundations laid for a great zinc smeltery far away in Siberia; and we have reason to believe that ere long a zinc smeltery may be erected at some seaport of India. In the meanwhile, the Japanese, with their customary adaptiveness, have inaugurated zinc smelting within their empire. There were, therefore, plans on foot that promised to make the art of zinc smelting one of far wider application than it had ever been during the century of its commercial history. These conditions were fully in evidence before the war began.

Germany, by virtue of its own great deposits of zinc ore in Upper Silesia and its contracts for the Broken Hill ore, was the great purveyor of spelter to the rest of Europe, especially to England. The first great consequences of the war were to suspend, to a major extent, the production of zinc ore in Australia, there being insufficient surplus smelting capacity outside of Germany and Belgium to receive it; and to throw a large part of the spelter requirements of Great Britain, France and Russia upon the United States, the result of which was to raise the price for spelter to a figure not previously recorded in many years. What other major and minor effects the disturbance of the war may have upon the spelter industry lie within the

sphere of prophecy. I will venture no more than the suggestion that they will be profound.

The world's great districts of zinc smelting have heretofore been Upper Silesia and Rheinland-Westphalia, in Germany; the valley of the Meuse and the Campine, in Belgium and Holland; and Kansas, Oklahoma and Illinois, in the United States. The art of zinc smelting was first introduced (from China) into Great Britain, but the British smelters have not, during the last 100 years, been leaders in the art; nor has zinc smelting attained great magnitude in their land.

During the last 50 years, there have been three types of zinc smelting (the earlier English and Carinthian processes having disappeared), which are known as the Silesian, Belgo-Silesian, and Belgian. In recent years, the Belgo-Silesian method has become known as the Rhenish, and this has shown a strong tendency to displace the Belgian process in Belgium and an even stronger tendency to displace the Silesian process in Silesia. The reasons for this are discussed in the metallurgical treatises, of which zinc smelting has recently acquired a rich literature. They may be summarized as a superior economy, as compared with the Belgian furnace; and, in Silesia, a change in the character of the ore which causes this method to be better adapted than the Silesian furnace. In the United States, the method of smelting is essentially the Belgian, which has been modified to conform to peculiar conditions.

Considering the art of zinc smelting upon its broadest lines, the variations between European and American practice are explained by variations in fundamental conditions, which may be summarized in the statement that in Europe labor is cheap and coal is dear; while in the United States, coal is cheap and labor is dear. Thus, we find American smelters striving ever for mechanical substitutes for hand labor, and European smelters aiming always to reduce coal consumption. There have been other determinative factors, the differences between which are, however, tending to disappear. One of these is permanence of the smelting districts. Another is scientific attention to the art.

Zinc smelting was begun in Upper Silesia in 1798 and on the Meuse in 1807, and ever since those dates, has been con-

ducted in those districts. Their metallurgical stability has induced operators to build substantially. From an early date, moreover, the smelting was directed by educated metallurgists, and both in French and German is there a literature extending backward for a century. In the United States, on the other hand, only two works, viz., those at LaSalle and Peru, in Illinois, have a long history, and, in the main, the zinc smelting industry has been characterized by shifts and uncertainties that stifled ideas of permanent building. About 1871, zinc smelting was begun at Pittsburg, Kan., and for 30 years was conducted with an absurd disregard of scientific control. Not until about 1898 were chemists employed, even to assay the ores bought and smelted. Ore was cheap, and for three decades the precept was "better butcher the ore than butcher the furnace". About 1901, most of the smelteries in this district were scrapped and the Iola district, where natural gas occurred, became paramount. Ten years later, Iola was the scene of deserted works and the star of Bartlesville and Collinsville, in Oklahoma, was ascendant, but even now it is waning and the great locus of zinc smelting is becoming the coal fields of Illinois and further eastward. With this last move, zinc smelters show that they are building for permanent business, not merely to reap some ephemeral natural advantage, and with the utilization of the services of metallurgists (which has been general only within the last 10 or 15 years), certain differences between European and American results are tending to disappear.

One other basic condition requires mention. European smelters operate generally in highly developed industrial regions, affording a market for sulphuric acid and rendering the free discharge of sulphur smoke unpermissible anyhow. Therefore, European smelters long ago began to make sulphuric acid as a by-product of blende roasting. American smelters, on the other hand, were able to emit their smoke without doing great harm and had no market for acid. Consequently, they did not make it. This condition, also, is undergoing radical change. Every smelter of blende east of the Mississippi River now makes acid.

In many respects, the development of the American zinc smelting industry has exhibited absence of initiative and curious contradictions. Our two great names are Wetherill and

Hegeler. The former invented the process of making zinc oxide direct from ore. The latter introduced the first successful mechanically-raked muffle furnace for blende roasting, modified the Belgian distillation furnace and introduced many mechanical contrivances. The best American zinc-smelting practice of the present day follows very closely in Hegeler's footsteps, with certain improvements borrowed from Belgium and Germany.

During the last 20 years, the vogue of the mechanical furnace for blende-roasting, in the United States, has become all but universal. At the present time our works have capacity for roasting about 800,000 tons of blende per annum, and only two or three examples of the old hand-roasting kilns survive. Yet, of our mechanical furnaces, the Hegeler dates back to 1884, and during the last 15 years there has been no introduction of any new type—an emphatic commentary upon the absence of originality that has, heretofore, characterized zinc smelting in America. In the meanwhile, the Germans have exhibited much alertness in developing and adopting mechanical roasting furnaces in spite of their lower rates of wages and consequent lack of incentive to substitute machines for men.

I may best elucidate further comparisons between European and American practice by sketching the principal parts of a modern zinc smelting works. In all of what follows in this paper, I have in mind only the smelting with coal-fired furnaces, dismissing from attention the smelting with natural gas in the United States, which is on the wane. Nor are the figures that I give intended to represent the practice with Silesian furnaces in Upper Silesia, Germany.

The ore is delivered into the works in railway cars, from which it is unloaded directly into the storage bins. The means for unloading, sampling, storing and reclaiming have, heretofore, been rather crude in many of the American works, but recently there has been an increasing tendency to adopt the superior methods that have long obtained among lead and copper smelters.

The ores coming to the zinc smelter are classified as calamine and blende. In Europe, the former is still calcined. In America, the calcination of calamine was abandoned by the

smelters many years ago, the advantages being pronounced unequal to the cost. Blende, of course, must always be roasted. In America, we use the Hegeler furnace if sulphuric acid is to be made; otherwise, simpler forms of mechanical furnace. Our object is mainly to save labor. In Europe, hand-raked furnaces of the Rhenania, or the later Delplace, type are commonly employed, which are both designed and operated to save coal. The dead-roasting of blende has been regularly effected with a coal consumption of only 10% of the weight of the ore, a lower figure than has ever been achieved in the United States. However, there is a growing usage of mechanical roasting furnaces in Europe and an adoption of such new and excellent types as the Merton and the Spirlet, which American smelters have not yet ventured to try.

The roasted ore goes to the mixer, where it is united with the proper proportion of reduction coal. Mechanical mixing and careful attention to this important part of the process were early practiced at LaSalle, but, elsewhere in the United States, this was generally done in ways far below European standards until recently. However, we are no longer subject to such a reproach.

Following European practice, our distillation furnaces are now commonly built entirely above the ground, the unclean, uncomfortable and unsanitary subterranean galleries of old being abolished. The Europeans are still ahead of us, however, in ventilation of the furnace houses. The Europeans generally lay out their furnaces in line. We lay them out in rows. The Europeans commonly employ recuperative (both reversing and counter-current) furnaces—again with view to economy of coal —and succeed in smelting a ton of ore with as little as a ton of coal. In the United States, we use mostly the long Hegeler furnace. With natural gas firing, there is no heat recuperation. With coal firing, the economizing of fuel takes the form of generating steam from the waste gases. The long furnaces and the steam boiler accessories are distinctly American, and both are due to Hegeler. To Hegeler also is due the charging car, metal drawing car, and other mechanical contrivances in aid of the work about the distillation furnaces. The only successful mechanical chargers, however, are of European origin; but a recent American invention of some promise is a mechanical dis-

charger. A distinctive feature of American distillation furnace practice is the use of blowers for the delivery of the combustion-air to the furnaces[1].

In the manufacture of retorts, the hydraulic press, which originated in Belgium, is now commonly employed both in Europe and America. However, the Europeans give more attention to the manufacture of their retorts and, unquestionably, make a better retort than we do.

In the handling of material in the works, the modern American plants are as well equipped with tramways, elevators, etc., as are lead smelteries of corresponding size. In this respect, our best American plants are in no wise inferior to the best European.

European smelters have long recovered lead and silver from their retort residues. American smelters now do so to a considerable extent, but the treatment of lead-bearing ores and recovery of the lead is less a feature of American practice than it is of the European. American zinc smelters pass the whole of their residue to the lead smelters. European zinc smelters commonly concentrate it by jigs and tables and deliver a lead concentrate for smelting.

Metallurgically, the essence of zinc smelting is the temperature of distillation. Speaking generally, the higher the temperature the better is the extraction of zinc. But with bad ores, and bad practice, high temperature is infeasible; for the furnaces and retorts will not stand it. A bad ore may be smelted with but little trouble, at a relatively low temperature, but the extraction of zinc will be poor. The aim of the zinc smelter is to smelt a bad ore and obtain the maximum possible percentage of zinc out of it.

In general, the Europeans excel the Americans in this respect. They mix their ores more scientifically, they make better retorts and they build stronger furnaces, all of which contribute to an ability to drive their furnaces at higher temperature

[1] Let it be noted that in offering these broad generalizations of comparative European and American practice, it is well in mind that there are representatives of several furnace types in the United States. Thus are to be found Siemens-Belgian furnaces at Peru and Depue, Overpelt-Rhenish furnaces at Pueblo, and counter-current recuperative furnaces at Palmerton.

than Americans have yet attained, and, at the same time, they manage with ores that are rather high in lead. In so smelting, they make a leady spelter, but a simple refining in a reverberatory furnace removes the excess lead. In only one American works is that practiced.

European smelters also generally recover blue powder as a commercial product. This is obtained from the prolongs, which condense a proportion of zinc that would otherwise be lost. American smelters do not use prolongs. Although in trials of them, an additional 1 or 2% of the zinc has been obtained, they have found it to be unprofitable—this again reflecting the difference in labor conditions.

I have outlined the main differences between European and American practice in zinc smelting. They are explained by the reasons previously mentioned. Per ton of raw sulphide ore, the American smelter uses about 2 to 2½ tons of coal and two or three man-days of labor; and extracts about 84 to 88% of the zinc that is in his ore; if he treats lead-bearing ore, he may recover 50 to 60% of the lead[1].

The European smelter uses about 1¼ to 1¾ tons of coal and 3 to 3½ man-days of labor; and extracts 88 to 90% of the zinc that is in his ore, and about 50 to 70% of the lead.

I hope to disarm criticism of these figures by stating that such figures properly should be accompanied by qualifications

[1] The matter of lead recovery can be but vaguely stated, it being so intimately related with the original content of the ore and the manner of effecting the recovery. The main sources of loss are, (1) by volatilization during roasting; (2) by volatilization during distillation, a portion of which may be recoverable by refining the spelter; (3) in the tailings of the mill, dressing the retort residues; and finally there are (4) the ordinary losses of the lead smelting furnace. As a debit against any lead that may be recovered under (2), is the cost of refining the leady spelter. Process (3) is a source of large loss and may be omitted, but then there is an increased weight of material to be treated by the lead furnaces and therefore a higher cost of smelting. Yet, here again there may be an offsetting condition, viz., the residues may be high in iron and the lead smelter may need iron. These few remarks will give an idea of the complexity of this subject, which is indeed incapable of accurate generalization. The only answer is that which is expressed in dollars and cents in each case. What applies to lead also applies to silver. In my generalizations of the requirements of coal and labor in zinc smelting, I have not included anything involved in the refining of spelter or in the treatment of residues remaining after zinc extraction.

and explanations that would run to pages in length and would constitute a condensed treatise upon the metallurgy of zinc; and that I offer the figures that I have used merely as broad generalizations for the purpose of exhibiting, in tabloid form, the lessons deduced from the differences in the art as practiced in Germany and the low countries and in the United States. They mean that the Europeans, with the aid of better furnaces and superior technical direction, are able to smelt more refractory ore than we Americans, and yet extract a higher proportion of the valuable metals. They have built more substantial plants—secure from fear of geographical migration of their industry—for the sake of increased durability and maximum economy of fuel. While the rates of wages are higher in the United States than in Europe, American zinc smelters have not been able to offset that by the development of superior efficiency, in the ways that the copper and lead smelters have done. Man for man, the German and Belgian smelter does as much work as the American. Thus, the attendance of the distillation furnaces in Rheinland and Belgium requires 1.75 to 2.5 man-shifts per ton of roasted ore, while in America the requirement is 1.75 to 2.25. The difference in labor in roasting is insignificant when mechanical furnaces are employed. Such economies in labor as America has effected have been chiefly in the handling of material, which, in zinc smelting, is a relatively small part of the process.

Before concluding this paper, I am bound to refer to certain misconceptions respecting the status of zinc smelting that continue to exist and the possibilities of any radical changes happening in this art, such as have happened in lead and copper smelting.

The art of zinc smelting is far from being at a standstill. When we find 1000 kg. of ore requiring 1000 calories of heat being distilled with 1100 kg. of coal equivalent to 8000 calories, as is done in the best practice, we are observing a thermal efficiency of 12½%, which compares favorably with good steam practice. When we find a ton of ore being smelted with 2½ man-days of labor, and consider that we are dealing with a concentrated product, and reflect that the total weight of material handled is relatively small and that the work on it from

step to step is often more cheaply done by a man than by a machine, we do not feel unduly mortified by our results. Nor does the extraction of only 85 or 90% of the zinc content of the ore shame us very much when we reflect upon the peculiar and troublesome metallurgical properties of zinc.

The so-called problem of the mixed sulphide ores that has engaged so much attention during 50 or 60 years is not a question of how such ores may be treated—for means have been known for a long time—but, rather, is it a question of how may such ores be treated with sufficient cheapness. This problem has been solved to a large extent by the improvements in the art of mechanical concentration (especially the flotation process) and the improved ability of the zinc smelter to treat plumbiferous and ferruginous ore. Yet, there are still ores whereof the beneficiation is highly unsatisfactory, such, for example, as those ores which contain fluorite and those ores which are a crypto-crystalline mixture of the component sulphide minerals. The present treatment of zinc ores that are high in silver leaves much to be desired. For some of these ores it is possible that hydrometallurgical or hydrometallurgical-electrometallurgical processes may be useful in certain cases. There has been a commercial hydrometallurgy of zinc for many years, but it has not been extensive, simply for the reason that most ores could be more profitably treated in other ways. The precipitation of zinc from solutions by electrolysis used to be troublesome and unsatisfactory, but now that seems to have been mastered.

Electric zinc smelting, which has engaged a good deal of attention during the last 15 years, is metallurgically of the same nature as ordinary smelting; the main difference is that, in one case, the zinc is distilled by the heat of the electric arc or the heat of electric resistance; while, in the other case, it is done by the combustion of coal. So far, electric smelting has become an art only in Sweden and Norway, where several thousands of tons of spelter are annually produced by this method. The smelters in Sweden and Norway enjoy very cheap power, whereby they have been able to overcome, or at least meet, the main obstacle that has heretofore prevented electric smelting from becoming a commercial art elsewhere.

Paper No. 191

THE DEVELOPMENT OF ZINC SMELTING IN THE UNITED STATES.

By

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The increase in the spelter production of the world during the last thirty years has been tremendous, and more than half of it has been in the output of the United States, which has increased its production more than all other countries together. But while the quantity of spelter produced by the country as a whole has increased enormously and very steadily, the production of the different smelting districts has varied widely.

The first spelter produced in this country was made by the United States Government, in Washington, D. C., in 1838, from ore from Franklin Furnace, N. J.—boulders of ore from the glacial drift in the Sparta Valley just south of Franklin, and ore from Perkiomen, Pa. The workmen were brought from Belgium, built the furnace, smelted the desired amount of ore, and returned to their own country. The spelter made was used to produce the brass for the standard weights and measures. The old pit at Franklin from which the ore was taken was known as the "weights and measures opening" until it was finally destroyed in the course of mining, about 1900.

The first serious attempt to make spelter in this country was by Joseph Wharton, in Bethlehem, using the oxidized ores of Friedensville. In 1856 or 1857, he employed Messrs. Matthiessen and Hegeler, two young German metallurgists who had just arrived in this country, to build a furnace. This was tried and abandoned, partly for the reason of a failure to agree with the designers, and partly for financial reasons. In 1859, Col. Wether-

ill, of zinc oxide fame, built a spelter furnace for him that was not successful. Finally, in 1859 according to some reports, and in 1862 according to others, Mr. Wharton brought to this country Louis de Gée, an engineer, and workman from Liège, who built and operated a plant that, with some interruptions, continued to make spelter until 1911. In the meantime, Messrs. Matthiessen and Hegeler had gone West, and after studying conditions there, built a works at La Salle, Ill., the nearest point in the then known coal field to the Wisconsin mines. In writing to one of the La Salle papers in June, 1910, immediately after the death of Mr. Hegeler, Mr. Matthiessen says:

> "The first shovelful of dirt was turned up December 24, 1858. We had a furnace running successfully when the Civil War broke out. There being no sale for spelter after the outbreak of hostilities, we ceased temporarily, but commenced operations again when in 1862 or 1863 a lively demand arose for zinc in the manufacture of arms and cartridges. During the cessation of manufacturing we had been making experiments, so that when we started again we did so with decidedly improved methods."

The credit for having first produced spelter on a commercial scale in the United States is, therefore, due to Messrs. Matthiessen and Hegeler.

The New Jersey Zinc Company at Newark, New Jersey, and the Passaic Zinc Company at Jersey City, New Jersey, built spelter works shortly afterwards. Several other small works were built in the East at various times, but none of them were important in quantity produced or length of life, except the works at Constable Hook, Bergenport, N. J. These works were operated more or less intermittently on the extremely pure ores of Friedensville, Pa., and were among the most important producers until finally closed in 1888, owing to the inability of the Company to handle the water in the mines.

In 1880, the works afterwards owned by the Bertha Mineral Company were started at Pulaski, Va., and were operated until 1911. The small works of the Wythe Lead & Zinc Company, at Austinville, Va., were only operated for a short time, and never produced much spelter. The most important works in the East is that of the New Jersey Zinc Company (of Pa.), at Palmerton,

Pa. This was started in 1898, and has been added to several times since. It is now practically the only producer of spelter east of the Alleghanies. The East has thus been a continuous producer of spelter from the beginning of the industry until the present day, and although relatively not as important as formerly, still produces a considerable proportion of the total.

The first district to take up spelter production was the Mississippi Valley, where Messrs. Matthiessen and Hegeler started their plant at La Salle, Ill., as already stated, and shortly after the Illinois Zinc Company started theirs at Peru, Ill., close by. Both works are still in operation and have been several times increased in size. In addition to spelter, both make sulphuric acid, and have rolling mills. They were followed by the Edgar Zinc Company, at Carondelet, Mo., in 1869, the Collinsville Zinc Company at Collinsville, Ill., in 1886, the Winona, in 1892, and some other smaller plants. In 1896 the development of the natural gas region of Kansas commenced, and no new works were built in the Mississippi Valley until the gas began to show signs of exhaustion. In September, 1906, the Mineral Point Zinc Company started its works at Depue, Ill., a few miles from La Salle and Peru. A little later the United Zinc and Chemical Co. built at Springfield, Ill., Hegeler Bros. at Danville, The Granby Co. at Rose Lake, and the American Zinc, Lead & Smelting Co. at Hillsboro. All are large modern plants, and have resulted in a tremendous increase in the production of this region. In 1882 the Mississippi Valley produced 21,000 tons of spelter. This had gradually increased to 62,000 tons in 1907, or about 200% in twenty-five years. In 1914 it was 135,000 tons, an increase of over 110% in seven years.

Before the Mississippi Valley smelters had been in operation for many years, the development of the Joplin district began, and before long the greater part of their ore was derived from this field. In 1878 the Cherokee Zinc Co. built its first plant at Pittsburg, Kans., near Joplin; and from 1878 to 1899, a dozen works were built at Pittsburg, Weir City, Cherokee, Girard and Bruce, Kans., Nevada and Joplin, Mo., by the Cherokee-Lanyon Co., Empire Zinc Company, Girard Zinc Company, S. H. Lanyon & Bro., Lanyon Zinc Company, Midland Smelting Company, G. E. Nicholson and the Rich Hill Mining and Smelting Company.

These works reached their maximum production in 1897 and 1898, and declined very rapidly after that, most of them moving to the natural-gas field. By 1903, nearly all had ceased operations, and practically no spelter was made in this region after 1908.

Messrs. William and Robert H. Lanyon built the first works in the natural-gas field at Iola, Kans., in 1896-7, and as soon as they had overcome the difficulties of working under the new conditions, they built a second works at the same place, and shortly afterwards, a third at La Harpe, a few miles to the east. In 1899, three more works were built, by other parties, in the same neighborhood, and one at Cherryvale, about 46 miles to the south. The development of this field was extremely rapid, and by 1901 it was the largest producing district in the country. Other works were built later in other parts of the Kansas gas field, but the immediate vicinity of Iola remained the largest producing point until the gas began to show signs of exhaustion; and from that time, production at this point declined rapidly until the present, when only one works is in operation at Gas City, between Iola and La Harpe, and one at Iola. In the meantime, other works had been built at other points in Kansas—Chanute, Altoona, etc.

In 1905 the first works in the Oklahoma field was built, and the output here increased more rapidly than that of Kansas declined; so that the capacity of the entire natural gas district increased until 1912, when it reached its maximum of 178,000 tons. During the past two years, it has dropped to 137,422 tons.

In the meantime, in 1892, works had been built in the Indiana gas field, at Ingalls and Marion. For a few years, they were quite important producers, but the gas did not last, and by 1904 they had practically ceased operations.

In 1903, the United States Zinc Company, an off-shoot of the American Smelting & Refining Company, built a plant in Pueblo, Colo., to treat the argentiferous zinc-lead ores of that region. It has been increased in size from time to time, its growth about keeping pace with that of the industry as a whole. It makes about 2.5% of the total production.

In 1904, the Grasselli Chemical Company built their first smelting works at Clarksburg, West Virginia. Later they built a second about 10 miles away, at Meadowbrook. Both have since

been added to several times. All of the ore is roasted at the acid plants of the Company, at Cleveland and other points, and shipped to West Virginia, where it is smelted with natural gas. The Clarksburg Zinc Company, in the same region, does not smelt ore, but makes spelter from galvanizers' residues. The American Zinc & Chemical Company started to build a smelting and acid plant at Langeloth, Pa., in 1913, to take the place of affiliated plants in the Kansas-Oklahoma field. So far, only the acid plant has been started. The production of this district has increased very rapidly, from 6000 tons in 1904 to 49,000 tons in 1914. It is likely to increase greatly in the future.

The East will remain an important producer for many years to come, although it is not likely ever to make a very large proportion of the total. Colorado and the extreme West are not likely to be much more of a factor than at present, unless a successful process of electric smelting or electrolytic treatment is discovered. It is not probable that smelting will ever be resumed in the Joplin region. The natural gas field has apparently passed its maximum and is likely to be of relatively much less importance in the future. The two localities that will probably supply the bulk of the spelter are the Mississippi Valley and the Pittsburgh district. The former has the advantage of nearness to the ore supply and cheap fuel; the latter is nearer to the market for both spelter and acid, and has close at hand a supply of better coal that can be used when the gas gives out.

EAST AND SOUTH.

As before related, the first works in the East was built at Bethlehem, Pa., about 1860. The first successful furnaces were of the ordinary direct-fired Belgian type, and some of them remained in operation practically unchanged until the works were finally abandoned in 1911. At first, the oxidized ores from Friedensville alone were used; later, blende from the same place and some from the West was treated; and, for several years before the works shut down, Willemite from Franklin. In 1889, an experimental gas furnace on purely German lines was tried and failed. In 1891, a Siemens furnace was built and continued in satisfactory operation until the works was abandoned. In 1896, a furnace of a modified Rhenish type was tried, and while it was

not entirely satisfactory, the experiments with it led Messrs. G. G Convers and A. B. De Saulles to the invention of their furnace, which is among the best now used. In the original Rhenish furnace, the gas was burned in a combustion chamber in the center, passed over the dividing walls and down past the retorts on each side to the regenerators. In the Convers-De Saulles furnace, the travel of the gas is reversed. It enters below the retorts on each side, goes up between them, over the partition walls, and out through the central chamber to the regenerators. Both furnaces heated the air only in continuous counter-current regenerators.

The first attempts to make spelter in this country, in 1848, at Newark, were not very serious or long-continued, as the attention of the Company was soon diverted to the manufacture of oxide of zinc, in which it was very successful. At one time, an English furnace for distillation *per descensum* was tried, but was soon abandoned. No definite records of this experiment remain, but the tradition of the works is that it was a man-killer. The first workable spelter furnaces were built in 1865, and were of the ordinary Belgian type—four in a block, with seven rows of eight retorts each. Later, they were replaced by longer and lower furnaces, two to a block, 20 retorts long and 4 or 5 high, with fireplaces at both ends. These were better adapted to the fine anthracite used as fuel. The fireplaces were narrow and deep and supplied with air by a fan; they acted as semi-producers and gave a very uniform distribution of heat with the lower furnaces. No ore was smelted at these works, but only refuse oxide and blast-furnace flue dust. They were finally shut down in 1897.

At Jersey City the first spelter was made in the early '70s, under the patent of Dr. Gideon E. Moore (U. S. No. 170,760. December 7th, 1875). The claim of the patent is rather curious:

> "The improvement in the art of distilling metallic zinc from its manganiferous ores, consisting of the treatment of the manganiferous zinc ore, supplementary saturating material and carbonaceous matter, simultaneously in the distilling vessel by heat, substantially as set forth".

The "supplementary saturating material" is "ferruginous, silicious or silico-ferruginous", depending on cost. The object of this addition being stated to be to prevent the corrosion and

destruction of the retorts. Strange to relate, the process is reported to have worked. The Passaic furnaces were of the ordinary Belgian type, but very high—in some cases, 9 rows. The works were finally abandoned in 1901.

The Friedensville ore was smelted for spelter at the mines and at Constable Hook, N. J. In both places the usual type of direct-fired Belgian furnace was used. Very little smelting was done at the mines and the works were abandoned about 1882. The works at Bergen Point (Constable Hook) were run for several years and produced an exceptionally pure spelter, but were finally closed and abandoned in 1888.

The Bertha Zinc Company built its plant at Martin's Tank, now Pulaski, Va., in 1880, and worked the silicate ore from its mines at Bertha. Three grades of spelter were produced, and the best ("Bertha") rapidly gained an international reputation for its purity and uniformity. The furnaces at this plant were of the Belgian type, but of English form. That is, they were higher than usual and had only one retort to a recess, instead of two, as is the general custom. All of the furnaces were in one building and were placed with their longer axes parallel to each other and at right angles to the longer axis of the building. The workmen were thus placed between two furnaces, a very hot and inconvenient arrangement. The practice at this works was extremely good, and the fuel consumption remarkably low for direct-fired furnaces. This latter was due to two causes—the excellent quality of the Pocahontas coal, and the water grates used. The latter were the invention of Mr. J. D. James, the foreman in charge. The consumption of coal per ton of ore was as low as 1.6 to 1.8 tons. The plant was finally abandoned in January, 1911.

The plant of the Wythe Lead and Zinc Company, at Austinville, contained only one block of two direct-fired furnaces of 140 retorts each, placed in 7 rows of 20 retorts. The 3 upper rows were 7¼″ in diameter and 47″ long; the lower rows were elliptical, 7⅝″ wide, 10″ high and 45″ long. Work was started in May, 1888. The ore was a low grade silicate from the company's own mine. The plant was operated until August, 1898, when the Wythe Company sold its entire output of ore to the Bertha Company at Pulaski, and stopped smelting. During the time it was in operation, it produced an average of 400 tons a year.

MISSISSIPPI VALLEY.

Smelting started in the Mississippi Valley at practically the same time as in the East, and for many years it was the largest zinc-producing district in the country. The present indications are that it will soon resume this position and probably hold it for many years to come. The first works was built by Messrs. Matthiessen and Hegeler, and to these two—especially to Mr. Hegeler—zinc metallurgy in America probably owes more than to any one else. In 1879, they patented their spelter furnace, which they have used successfully ever since, and which is now used with satisfaction by many of the latest plants, and was the model from which the natural-gas furnaces were designed. These furnaces are very simple, consisting merely of a long chamber holding the retorts. The gas is all admitted at one end, and the air is gradually admitted through ports equally spaced lengthwise of the furnace. It is low in first cost, economical in labor, and does excellent work, but is very extravagant in fuel. For Messrs. Matthiessen and Hegeler's purpose, the latter was not an objection, as their works are located directly over their own coal mines, and the mine cars are dumped directly into the producers. The waste heat from the furnaces is completely utilized in making steam, all that can be produced being used for the spelter plant, coal mine or rolling mill.

Possibly the most valuable of Mr. Hegeler's inventions was his roasting furnace, patented August 12, 1884, and now used, with slight modifications, by every smelter in this country that makes acid. These furnaces are 7 hearths high and built in pairs. The ore is moved by rakes, which are drawn through by rods pushed in from the opposite end. The rakes are pulled through the hearths of one furnace and delivered on turn-tables at the opposite end. When a round is completed the turn-tables are reversed and the same rakes drawn through the hearths of the other furnace, the ore traveling in opposite directions at the same level in the two. The furnaces are usually 80 ft. long and the hearths 6 ft. wide. A pair of furnaces roasts from 40 to 50 tons per day.

In addition to the spelter and roasting furnaces which are so generally used, Mr. Hegeler, either alone or in conjunction with his partner, Mr. Matthiessen, patented or introduced many

minor improvements in zinc smelting which have since been very generally adopted. In 1873, they patented their first roasting furnace, which, although they did not continue to use it, has since been very successful at Ponte di Nossa, Bergamo, Italy, under the name of the Cermak-Spirek furnace. Mr. Hegeler was the first to mix charges mechanically, and also made the first cars for charging, cleaning, and metal drawing. His works showed many evidences of his thought and care for the safety and convenience of his workmen many years before the "Safety First" movement was thought of. Mr. Hegeler patented a gas producer that is largely used, and several modifications and improvements in his spelter furnace. His sons, Herman and Julius W., have also taken out several patents for improvements in both spelter and roasting furnaces.

The Illinois Zinc Company, at Peru, started with direct-fired Belgian furnaces, but later built a Siemens furnace, with which they did not have great success. The superintendent of the works, Mr. C. F. Neureuther, however, patented a modification of it* (No. 666390, January 22, 1901), having two or three rows of ports. With these furnaces, the Illinois Zinc Company have been very successful, and have replaced all of their direct-fired furnaces with them. This plant uses the Matthiessen & Hegeler roasting furnaces and has a chamber acid plant and a rolling mill.

The other earlier works in this region were all small and equipped with the usual direct-fired Belgian furnaces.

The first of the newer works in the Mississippi Valley was the Nassau plant of the Mineral Point Zinc Company, at Depue, Ill. At the start, it consisted of three Siemens furnaces of the Neureuther type, containing 800 retorts each, Hegeler roasting furnaces and a Schroeder contact acid plant. Later a Matthiessen & Hegeler spelter furnace was tried but abandoned on account of its high coal consumption. This plant has been enlarged several times and now contains 12 furnaces, with a total of 9080 retorts and proportionate roasting and acid capacity.

The American Zinc, Lead & Smelting Company's plant, at Hillsboro, Ill., has five blocks of two furnaces each, of the Hegeler type, with a total of 4000 retorts. Waste-heat boilers of sufficient capacity to supply all the steam required by the works, are con-

* This patent was later declared invalid by the courts.

nected to the furnaces. The ore is roasted in two Hegeler furnaces with hearths 70 ft. long and 6 ft. wide. There is a chamber acid plant using all of the gas made by the roasting furnaces. At this plant arrangements have been made for storing the coal supply under water. This prevents the rapid deterioration which takes place when the Illinois coals are kept in piles in the open air. Nearly all of the ore is concentrates from the company's own mines, much of which arrives at the works wet, and frequently frozen. Excellent arrangements have been made for thawing such ore by placing the cars in the ore house over concrete tunnels heated by the waste gases from the roasting furnaces.

The Rose Lake smelter of the Granby Mining and Smelting Company, just outside of East St. Louis, Ill., is one of the latest and best arranged plants in this region. It has four Siemens furnaces with 810 retorts each, supplied by two batteries of Hughes producers. The plant has two Hegeler roasting furnaces and two well-equipped chamber plants arranged so that they can be worked separately or in series. The roasting furnaces are supplied with gas by a single 10-ft. Chapman producer. The plan of the works provides for extensions of all departments without interfering with the present excellent arrangement.

The works of the National Zinc Company, at Springfield, Ill., was built by the United Zinc and Chemical Company. It contains Hegeler furnaces and treats ore roasted at the Argentine plant of the same Company.

The works of Hegeler Bros., at Danville, Ill., is equipped with Hegeler spelter furnaces, roasting furnaces and a chamber acid plant.

All of the later works in the Mississippi Valley are well-constructed permanent plants. The buildings are mainly of steel and concrete, and in nearly all cases the furnaces are elevated, keeping the regenerators (when used) above ground. All refuse is discharged into hoppers under the working floor and removed by cars. Most of the potteries are equipped with hydraulic presses, and many have separate small dry rooms with adequate arrangements for heating and ventilation.

The tendency in the West has been to build very large furnaces, the advantages claimed being lower first cost and less producer labor. It is doubtful whether these offset the greater diffi-

culty in controlling the distribution of heat and the loss occasioned when such large units go wrong. In working a variety of ores, small furnaces are more economical, as the necessary experiments to determine proper conditions can be made on a smaller and less expensive scale. In the East, small furnaces have always been the rule. The Convers-DeSaulles type are necessarily quite small, and where Siemens furnaces are used in the same plants, it has been found advisable to build them all the same size.

MISSOURI-KANSAS COAL FIELD.

There were formerly a number of works in Southwestern Missouri and Eastern Kansas. Nearly all were similar in style, having direct-fired Belgian furnaces built in blocks of two, each block being in a separate building. Each furnace building, with its two furnaces, was placed on an artificial mound, leaving very deep ash pits open at both ends. The grate bars were 7 or 8 ft. above the ground level, and the fires were cleaned by a man standing on the ground below. There were usually only two grate bars made of a long "U" of 1″ pipe, the ends of which were connected respectively to the top and bottom of a water barrel standing on the furnace floor, about 3 ft. above. This provided a circulation of water that kept the bars cool enough to give them a very long life. Shortly before the works in this district were abandoned, some of the plants tried the experiment of heating two furnaces by one fire. The deep grate acted as a gas producer, and the side of the furnace directly over it was heated largely by radiation. The gases passed over the center wall, at the top of which additional air was admitted which burned the gas in its passage down the opposite furnace. The plants using these furnaces reported a considerable saving of coal by their use, the decrease varying from 25 to 35%. There was, however, considerable difference of opinion regarding the recovery of metal, some works saying it was not affected, while others claimed that it was reduced enough to offset the saving in coal and labor. Their use never became general.

Both the Granby Mining and Smelting Company, at Pittsburg, Kans., and the Rich Hill Mining and Smelting Company, at Rich Hill, Mo., tried Siemens furnaces in 1882, but neither of them found them satisfactory, and they were abandoned.

All of these works used high grade Joplin blende, roasted mainly in two- or three-hearth reverberatory furnaces. The Pearce-Turret Furnace and the Holthoff-Wethey Furnace were tried and gave fair results in Joplin. No use was ever made of the gas.

Most of the smelting in this district was done by small concerns with inadequate working capital, and much of the work was of a very happy-go-lucky character. It was not unusual for a company to buy ore on Monday, smelt it, and sell the product sight draft on bill of lading, to get the money to pay for the ore on Saturday night. In the old days in Joplin, it was customary for everyone to settle all debts on Saturday night, and the banks kept open until ten o'clock to facilitate payments. All work stopped, and everyone lined up on the main street to watch fights, which were fairly numerous. If a man could not pay up on Saturday, it was advisable in the interests of his own longevity that he should leave town at once and stay away.

This district reached its maximum production in 1898 and declined very rapidly in the next few years, owing to the competition of the natural gas field. Since 1902, practically no spelter has been made in what had been the principal producing district from 1888 to 1898.

KANSAS-OKLAHOMA GAS FIELDS.

All of the plants in the natural-gas field smelt both oxidized ores and blendes. The former are not calcined, as they vary constantly in the relative proportion of carbonate and silicate to such an extent that it has not been found profitable to do so. The sulphides are, of course, roasted, but only one works in this district ever utilized the gas. The United Zinc and Chemical Company, at Iola, had a chamber plant and made acid as long as the plant was in operation. They also had an acid plant at Argentine, Kans., where they roasted part of their ore. At both plants, they used the Hegeler furnaces. Several of the works used three-hearth reverberatories, built either 8 or 16 in a block, in which they roasted more ore per man and less per square foot of hearth than in any hand-furnace worked. The practice was peculiar. A charge was spread on the upper hearth and

left there for 12 hours, with very little raking. It was then split and spread on the two lower hearths and kept for another 12 hours. The layer of ore was very thin and a minimum of labor gave it the necessary amount of turning over to effect the roasting in a reasonable time. These furnaces were very lightly built and their cost was trifling. The small output per furnace was, therefore, not a serious detriment.

The Lanyon Company used Ropp furnaces until prevented from so doing by a court order in an infringement suit brought by the owners of the Brown patent. They then changed to the Cappeau furnace (patented 1902), which is similar to the Ropp in operating mechanism, but is supported on a steel framework instead of masonry. The Edgar Zinc Company, at Cherryvale, have always used the Brown Horseshoe furnace. Most of the works now in operation use either the Cappeau or Zellweger, both of which do good roasting and are economical in labor, but are very extravagant in fuel. It is claimed that recent improvements in the Zellweger have greatly helped in this respect. The Prime Western Spelter Company at one time had some Greenawalt furnaces, but they are no longer operated.

All of the works in the Kansas-Oklahoma district use furnaces that are a modification of the Hegeler. They are built in blocks of two, back to back, and both gas and air are admitted at alternate buckstaves for the greater part of the length of the furnace. This arrangement was patented by R. J. & W. Lanyon, December 27, 1898, and by W. & J. Lanyon, March 21, 1899. The gas travels lengthwise of the furnace, and none is admitted to the quarter nearest to the stack. The furnaces are usually large, containing 300 to 400 retorts each. A few of the works have what are called "half-blocks", that is, furnaces of half the above length. The Tulsa Fuel and Manufacturing Company, at Collinsville, Okla., tried some furnaces patented by Mr. C. A. H. De Saulles, October 22, 1912, in which the ore and gas enter under the retorts and pass out through a hollow backwall. The retorts in these furnaces face both ways and there is but one furnace to a block. The air and gas for each port could be regulated separately from outside the furnace. So far they have not shown sufficient advantage to lead to their general adoption. The United Zinc and Chemical Company, at Iola,

experimented with a regenerative gas furnace, but the results were not encouraging and it was abandoned. Since the gas has become scarce, some of the Kansas plants have experimented with the use of oil as fuel. They have succeeded in developing an arrangement of burners that would work, but the price of oil has been too high to permit of its general use.

At the start, the gas plants smelted Joplin ore almost exclusively, but the rapid increase in the demand soon raised the price to a prohibitive point and smelters turned to other sources.

The first ores tried were the comparatively lean ferruginous blendes of Colorado, and much trouble was experienced in working them. Benjamin Sadtler, of Denver, Colo., patented a retort with a basic lining, in February, 1900, which was at first reported to greatly improve the work with these ores. It, however, soon became known that successful working depended mainly on proper temperature regulation, and the low grade ferruginous blendes were soon treated successfully by all the smelters with their ordinary equipment. A little later, carbonates and silicates from Mexico were used in considerable quantities, until a change in the tariff, imposing a prohibitive duty, prevented their importation. Since the last revision of the tariff, which reduced the duty, very little has been imported owing to the disturbed political conditions in Mexico. For the past few years, large amounts of carbonates and silicates from New Mexico, Arizona and Colorado, have been used—partly on account of their relatively low price, and partly to save gas, as they do not require roasting. Quite recently, blende from Butte, concentrated by flotation, has been used by some of the works. Its extreme fineness is reported to have caused considerable trouble.

COLORADO.

Colorado was the first of the Western States to produce spelter, the United States Zinc Company starting its works in Pueblo, June 9, 1903. The plant originally had three Overpelt furnaces and these have since been increased to seven, with a total of 1704 muffles.

The Overpelt furnaces are provided with alternating regenerators and have but three rows of large muffles. The original furnaces at Pueblo followed the European practice of

using large condensers fixed in place in the upper part of the retorts. The charge was introduced through the condenser and the residues were removed through an opening under it. This practice has been abandoned and small condensers are now used, which are taken down for charging and cleaning, as is usual at the other American works. One of the principal improvements made at these furnaces was the introduction of ladle cars for drawing metal instead of the hand ladles formerly used.

The ores are mainly silver-bearing sulfides, which are roasted in a Hegeler furnace. They are usually low in zinc and the lead and silver are really the main products.

PITTSBURGH DISTRICT.

The first plant in this district was that of the Grasselli Chemical Company, at Clarksburg, W. Va., built in 1904. This plant has Lanyon-Hegeler furnaces similar to those used in Kansas and Oklahoma. All of the ore for this plant is roasted, and the gases utilized, at the various acid plants of the Company at points in Ohio and Pennsylvania. This plant has been added to until it has reached the maximum possible at this location, and the company has since built a second similar plant, at Meadowbrook, W. Va.

The Clarksburg Zinc Company, also, has a plant at Clarksburg, but does not treat ore, all of its spelter being made from galvanizers' residues. The furnaces are of the usual natural-gas type.

The new plant of the American Zinc & Chemical Company, at Langeloth, Pa., about 30 miles from Pittsburgh, has been making acid for some months and will probably be producing spelter before this is in print. At present, the plant consists of four Hegeler furnaces, each containing 864 8-inch retorts. There is a single furnace to the block, with a center wall and six horizontal rows of retorts on each side. Each furnace is in a building by itself and has its own Hegeler producer. The ore is roasted in Hegeler furnaces, the gases being utilized in a chamber plant. The company owns its own coal mine and the plant is located directly over it. The intention is to sell the lump coal and use the slack for fuel. All of the waste heat of the furnaces will be utilized for making steam for power, with

the expectation of selling what is not required for the operation of the plant. The plan of the works allows of increasing the size four-fold without departing from the present excellent arrangement.

The Prime Western Spelter Company has built an acid plant at Tiltonville, Ohio, about 40 miles southwest of Pittsburgh and 8 miles north of Wheeling, W. Va. At this plant, they are roasting blende in Hegeler furnaces and making acid by the Schroeder contact process. The roasted ore is shipped to other points to be smelted.

ROLLING MILLS.

The first zinc rolling mill in this country was built by Messrs. Matthiessen and Hegeler, at La Salle, Ill., in 1868, and has been in operation ever since. It has been repeatedly re-designed and rebuilt and has always been maintained in a highly efficient condition.

The Illinois Zinc Company built its mill in 1882, and has always been a close competitor of Matthiessen & Hegeler. Its mill has also been changed a number of times to keep pace with improvements.

The Lanyon Zinc Company built a rolling mill at La Harpe, Kans., in 1902. It was radically different from any other zinc mill in the world, having been designed on the lines of the Pittsburgh Tin Plate Mills, and did not prove to be a success. It was abandoned some years since. Later, a small mill was built at La Harpe, to roll narrow strips of zinc for the manufacture of fruit jar covers. It was finally taken over by the principal customers, Ball Brothers, and moved to Muncie, Ind., where it is still in operation. Most of the brass companies occasionally roll some zinc, but none of them do so regularly.

The Lehigh Zinc Company built a rolling mill at Bethlehem, in 1865, and operated it until 1877 or 1878. About this time the works changed ownership and rolling was never resumed. The Passaic Zinc Company built a small mill at its Jersey City plant, but did not operate it for any length of time.

John Davol & Son operated a small zinc rolling mill in Brooklyn for several years. They made a specialty of etchers' plates and their product was of the highest quality. Their

practice was peculiar in some important respects. The slabs were cast in closed moulds and were shorter, wider and thicker than usual. They were roughed in the ordinary manner and then planed on both sides by a special machine having a knife wider than the slab, so as to take a thin slice off the entire surface with a single cut. The planed slabs were then finished, polished and cut to size. In 1897-98, German plates of inferior quality, but much lower price, appeared on this market and soon drove out Davol's product; the newspapers, who were the principal users, being willing to accept the lower quality in consideration of the lower price. Davol was not willing to meet competition on these terms and shortly afterwards retired from business.

OXIDE OF ZINC.

An entirely new process of making oxide of zinc direct from the ore was invented in this country in the early '50s, and three patents were taken out in 1855, by Jones, Burrows and Wetherill, on almost identical lines. Jones was an officer of the New Jersey Zinc Company; Wetherill was the Superintendent of the Paint Grinding Department of the same Company; and Burrows was a workman employed by the Passaic Chemical Company, whose works adjoined those of the New Jersey Zinc Company, and some of whose furnaces were on its property.

At that time the New Jersey Zinc Company had recently started the manufacture of oxide of zinc, using reverberatory furnaces and muffles, neither of which was very satisfactory. Burrows states that one night the flue from one of the furnaces that he was attending leaked, and he covered the hole with a piece of grate bar, throwing a shovelful of refuse on it. The refuse proved to be a mixture of coal and zinc ore, and the heat of the flue being sufficient to light it, Burrows soon noticed a cloud of zinc oxide coming off. He built a small furnace and repeated the experiment, and when he found that it worked again, showed it to the officers of the New Jersey Zinc Company, among whom were Wetherill and Jones. The grate bars used were what are now usually called "Wetherill grates", but were in common use for boiler firing at that time in the vicinity of Newark, where they were made by Renton, who had a machine-shop and foundry. Col. Wetherill frequently stated that

he had nothing to do with the invention of these grates, but his name has been persistently attached to them.

Col. Wetherill proposed to Burrows that they work up the invention together, as Burrows had not the money to do so alone, but the proposition was declined, and each went ahead on his own account. The result was that three people applied for and obtained patents for substantially the same thing in the same year. Wetherill also took out patents for improvements in 1855-6-7-9 and two in 1868. The New Jersey Zinc Company acquired the patents of Jones and Burrows, but could not agree on terms with Wetherill. The latter shortly afterwards sold a license to use his process to the Passaic Zinc Company. Both the New Jersey and the Passaic Companies put the process in operation, as it proved to be a great improvement on those previously used. Everything went quietly until the Wetherill patent had nearly expired, when he brought suit against the New Jersey Zinc Company for infringement and accumulated profits. The suit that followed was long and hotly fought on both sides. The final decision of the court was that the furnace was Burrows' invention and the process Wetherill's and that half the profits were due to each. As the Zinc Company owned the Burrows' patent, it was obliged to pay half the increased profit due to the use of the invention, to Wetherill. The decision seems a very fair one, as while the original idea appears to have been Burrows', he had not sufficient knowledge or skill to develop it and make a working process of it. The latter was done by Wetherill, who gave much time and work to the perfection of the detail and practice of the operation, and certainly deserved the credit of making it the success it has been. At the present time, every works in this country, but one, uses the Wetherill process. The much lower cost by it and the possibility it gave of profitably working low grade ores have been the main causes of the tremendous increase in the oxide business of this country, which now produces considerably more than half of the world's supply.

The method of collecting oxide in bags was invented by S. T. Jones, of New York, in 1852, and is now universally used, not only by all of the oxide plants in this country, but by many other smelters. Numerous patents have since been taken out for variations of this process.

The practice of oxide-making has improved greatly in recent years. Much larger furnaces are used, more material is treated per square foot of grate, better recoveries are obtained, and the quality of the product is under closer control. These improvements are due to a better understanding of the chemistry of the process, better mechanical arrangements, and closer supervision. There have been no radical changes since Col. Wetherill's day, but he would hardly recognize the later plants, as the changes in almost all details have completely altered the general appearance. It is difficult to give credit for these improvements, as almost everyone who has been closely connected with the manufacture has done something, and while the total result of the changes is large, it is impossible to say how much of it is due to any particular one.

The Florence plant of the New Jersey Zinc Company (of Pa.), is the only one that uses the French process of distilling and burning metallic zinc. The same company has two plants at Palmerton, Pa., which are by far the largest in the world. The older, or West Plant, contains 34 blocks of oxide furnaces, and the new, or East Plant, 20 blocks. Each block is an independent unit, with its own blower, exhaust fan, and bag room. These plants treat only the ores from Franklin furnace, and make an oxide containing only a small fraction of one per cent of lead. It is used mainly for paint and rubber goods.

The works of the Mineral Point Zinc Company, at Mineral Point, Wisconsin, treat the local ores and those from other Western States. As these ores always contain lead, the resulting oxide contains from 3 to 20% of lead sulfate. It is used almost entirely for paint. The works was completely rebuilt in 1911 and now contains four independent units.

The plant of the Ozark Zinc Company, at Coffeyville, Kans., was built to treat the oxidized ores of New Mexico, but of late years has used more of the low grade sulfides of Colorado. The oxide is of the same character as that made at Mineral Point.

The small oxide plant of the Bertha Mineral Company, at Austinville, Va., was built on the same lines as the others, to treat the local ores, making an oxide containing from 20 to 30% of lead sulfate. This plant has hardly passed the experimental

stage, but it is making a good product and is likely to be of more importance.

For many years the demand was entirely for an oxide as free from lead as possible, and the rubber trade still requires an oxide of this character. Of late, the paint grinders have found that a mixture of pigments gives a better paint than any single one, and the demand for leaded oxides is increasing, as the presence of lead sulfate gives greater body and presents certain advantages in grinding qualities. At the same time, the lead being present as an insoluble sulfate, is not as poisonous as the basic carbonate, and not liable, like it, to be discolored by atmospheric agencies. The production of an oxide of good color from leaded ores, is, however, very much more difficult than when the ores are free from lead, and as color is a most essential quality, this has caused the failure of several attempts to make a pigment oxide from lead-bearing ores.

A number of wet processes have been proposed for the manufacture of pigment oxides, but none have succeeded, as aside from the high cost, none have made an oxide having the necessary physical qualities.

ORE CONCENTRATION.

The greater part of the zinc ore produced in this country is concentrated by the usual wet methods, with jigs and tables. The Joplin district has developed a practice of its own, in which the unsized ore is first treated in roughing jigs, making tailings clean enough to be thrown away. The Hutch products are retreated on finishing jigs, making a very clean concentrate, and the tailings are cleaned up on tables. Of late years, some of the larger mills have added tables to their equipment to save part of the fine ore formerly lost. The work of this district has improved greatly in recent years, but owing to the low grade of the ore mined (3 to 5% blende), the losses are necessarily large. The average zinc recovery is 60%; lead recovery, 85 to 90%.

Up to about fifteen years ago, all of the ore in Wisconsin was prepared by cobbing, or hand-jigging. At present it is treated at the mines, much as in Joplin. Sometimes the product from the jigs is rich enough to ship, but in many cases it con-

tains too much pyrites, and is then treated on magnetic separators after a partial roast. The greater part of the iron can be removed in this way, giving a very high-grade product. A Custom Plant using the Huff electrostatic process was formerly operated at Plattville, Wis., but burned down, October 21, 1911, and has not been rebuilt.

Shortly after the mines at Franklin and Sterling Hill, N. J., were opened, attempts were made to separate the different minerals, but they were not continued, as the operating companies found the unseparated ore was suitable for the manufacture of zinc oxide.

About 1890, Messrs. J. P. Wetherill and G. G. Convers, of the Lehigh Zinc & Iron Company, again attempted the separation, and this time with complete success. Their first method was to heat the ore to a very moderate temperature and separate on Wenstrom machines. This was patented by Mr. Convers, December 20, 1892. They were not entirely satisfied with this method and continued their experiments, which resulted in the discovery, by Mr. Wetherill, of a new principle in magnetic separation—that of producing a highly concentrated field by using pointed pole pieces. Mr. Wetherill took out three patents on March 3, 1896, for the general principle, for the application of it to ores containing Franklinite, and for the machine. A mill was built, and the Willemite separated was used for the manufacture of spelter, and the Franklinite for oxide, with a considerable increase in profits. Experiments were continued, and September 28, 1897, Mr. L. G. Rowand patented an improvement in the machines, and March 7, 1905, another, which greatly increased the efficiency and has entirely displaced the earlier types in this country. In the earlier machines, both poles of the magnet were on the same side of the feed belt, with the result that less than half of the field was operative and the strongest part of it did no work. In Mr. Rowand's improvement, one pole is placed above the belt and one below; the former is pointed, the latter blunt. The entire field is thus available and the maximum possible lifting effect is utilized.

These machines are used for all of the ore at Franklin, and a number of points in the West. Many of the blendes of the far West contain a large amount of isomorphous iron and can be

lifted away from the associated pyrite and galena by the powerful magnets of the later Rowand machines.

February 26, 1901, Lucian I. Blake and Lawrence N. Morscher took out the first patents for the electrostatic separation of ores. They found that different minerals were charged with opposite polarity when brought near a highly charged static conductor, with the result that certain ones were attracted by it and others were repelled. As blende and pyrite were affected in opposite ways, a method of separation was based on this principle. This and later patents by the same parties were eventually acquired by the American Zinc, Lead and Smelting Company, who also bought the patents for a somewhat similar process, by Messrs. P. H. Wynne (November 28, 1905) and Millard Woodsome (September 25, 1906), both of which had previously been assigned to Mr. Charles H. Huff and which are the basis of what is known as the Huff Process. The American Zinc, Lead and Smelting Company and its affiliated companies have built a number of mills using these processes, and state that they are giving very satisfactory results.

Other electrostatic methods have been patented by H. M. Hutton and W. L. Steele, C. S. Dolbear and A. H. Perry; but none of them have been largely used.

The successful application of flotation to the separation of blende by the Butte & Superior Company is the most recent advance in concentration in this country. They have been followed by others and the indications are that this method will render available a large amount of ore that was of too low grade to be smelted without concentration and could not be treated successfully by the older methods. This method is of particular value for slime concentration.

IMPROVEMENTS.

Two types of spelter furnace have been developed in the United States. The Hegeler, which was later modified by the Lanyon to suit the conditions of the natural-gas field, and with which by far the largest part of the smelting capacity of the country is equipped. The Convers-De Saulles furnace has done excellent work and is much more economical in fuel than the

Hegeler. As the patents covering this furnace are owned by one company, it has never come into general use.

Messrs. Convers and De Saulles also patented a process of producing zinc dust, which makes a much better quality of product than the ordinary prolong blue powder, and at a very moderate cost.

Several roasting furnaces have been successful to a greater or less extent; the Hegeler, Brown, Ropp, Pearce, Cappeau, Zellweger and Greenawalt have all done satisfactory work in the natural-gas field, but most of them are not adapted for plants making sulfuric acid, as the gases are too dilute. The Brown Muffle Furnace has been successfully used in Silesia, in plants making acid. The Hegeler was the only one originally designed to give a gas suitable for acid making, and is the only one used for this purpose in this country.

Several forms of ladle car, for use in drawing metal, have been invented and have done good work. The most important are, first, the Hegeler, patented December 27, 1881; and, second, the Chapman, the invention of Mr. C. S. Chapman, of Pittsburg, Kans., patented July 22, 1900. The Hegeler apparatus consists of a four-wheeled truck, running on tracks on the floor in front of the furnace, and carrying a ladle hung from a crane, which is raised and lowered by a winch. A shield on the side of the car next the furnace protects the workmen. The Chapman car is a wide shield hung from rollers, traveling on an overhead rail, and having a vertical slot at the center opposite a ladle that is raised and lowered by a winch. Both are largely used and have given satisfaction. August 9, 1881, Hegeler patented the first cleaning car. It has a shield to protect the men and grooved rollers opposite each row of retorts on which to rest the scrapers. The whole apparatus is carried on a car running on tracks in front of the furnace. In 1899, William and Josiah Lanyon patented a shield traveling on an overhead rail and having openings opposite each retort for the cleaning tools; it also carries a drawing ladle. Various other forms of shield are in common use.

The method of cleaning retorts by blowing out with steam or water was developed by the Missouri-Kansas coal smelters, and is in very general use. It saves labor but does not clean the

retorts as well as hand work. The amount of steam or water used is very small and the practice, contrary to what might be expected, does not injure the retort.

Of gas producers there is no end, but very few have been invented or developed by the zinc smelters. The Hegeler producer was designed especially for use with the Hegeler furnace, and in that connection has done good work, but has not been much used for other purposes.

Several charging and discharging machines have been patented and tried. The Queneau, in which the charge is batted into the furnace by the arms of a rapidly revolving fan wheel, and the James, in which the charge is blown into the retort, both charge the retorts well, but their use did not cause sufficient saving in time or cost to warrant their continued use. The Simmonds' discharging machine, patented September 8, 1914, has a scraper chain introduced into the retorts and is reported to work well, but has not had time to come into general use.

NEW PROCESSES.

No new process of making spelter has come into commercial use, although many experiments have been made.

The hydro-metallurgic processes fall into three groups, according to the solvent used. These are acids, chlorine, and ammonia. Several processes have been patented and tried using acids, but none have been profitable, and I do not know of any that are even being experimented with at present. The main troubles are the large excess of acid necessary to dissolve the zinc completely, the large amount of other metals dissolved at the same time, and the expense and difficulty of purifying the solutions.

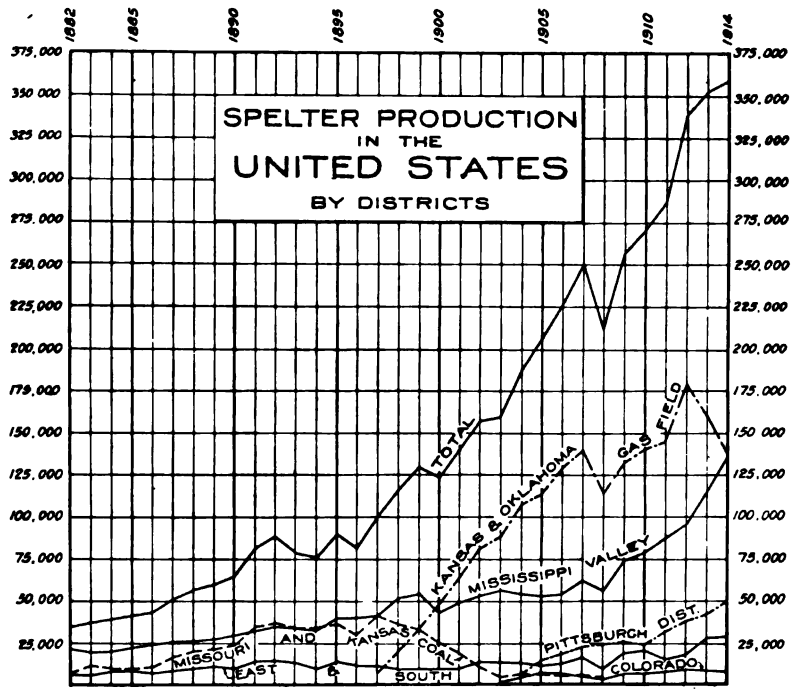
The second group of processes, using dry chlorine, is being tested by several people. The basic idea of such a process is old and well-known, but various modifications, as those of Baker-Burwell, Malm, and the Northwestern Metals Company, are being tried on a fairly large scale, and in each case the inventors claim with good results, but so far they are not commercial. They are subject to the same disadvantages as the previous class, with the added drawback of using an expensive, volatile and very poisonous solvent.

Mr. Bretherton has recently taken up the old ammonia process and the published results of his experiments show very good extraction. He has devised some very ingenious apparatus to prevent the loss of ammonia (which was one of the causes of previous failures) and has succeeded, on a small scale, in working with very slight losses. Ammonia, as a solvent, has the advantage of not dissolving the carbonates of lime and magnesia, which are a serious cause of expense when acids or chlorine are used. It dissolves the zinc, copper and cadmium, and small proportions of the iron and nickel; the two latter sometimes in sufficient proportion to discolor the zinc oxide precipitated from the solutions. The solvent is, however, expensive and so volatile that great care has to be exercised to prevent excessive loss. The Bretherton process has not yet been tried on a manufacturing scale.

Some experimenting has been done with electrolytic precipitation, but it has not been successful and it is exceedingly doubtful if it ever will be so in a commercial sense. There is, first, the difficulty and expense of making and purifying the solutions; second, the difficulty of continuously making a solid and coherent deposit; and third, the cost of the power required for the precipitation. The possible minimum of the latter is well known, and no district is known in this country in which both ore and power can be obtained cheaply enough to offer much prospect of success.

Much work has been done, and many patents have been taken out, for furnaces and processes for the electrothermic smelting of zinc. Mr. Woolsey McA. Johnson has unquestionably made more progress in this direction than anyone else, and even he is now confining his attention to ores containing other valuable metals besides zinc. That an electric smelting process can be worked out, no one doubts. So far the power requirements are too high and the difficulties in condensation have not been overcome. With larger and better furnaces, the former will doubtless be reduced and means will probably be discovered of avoiding the excessive production of flue dust and blue powder. The information available at the present time does not indicate that electric smelting, purely for the production of spelter, is likely to be a serious competitor of coal or gas smelting. In the case of

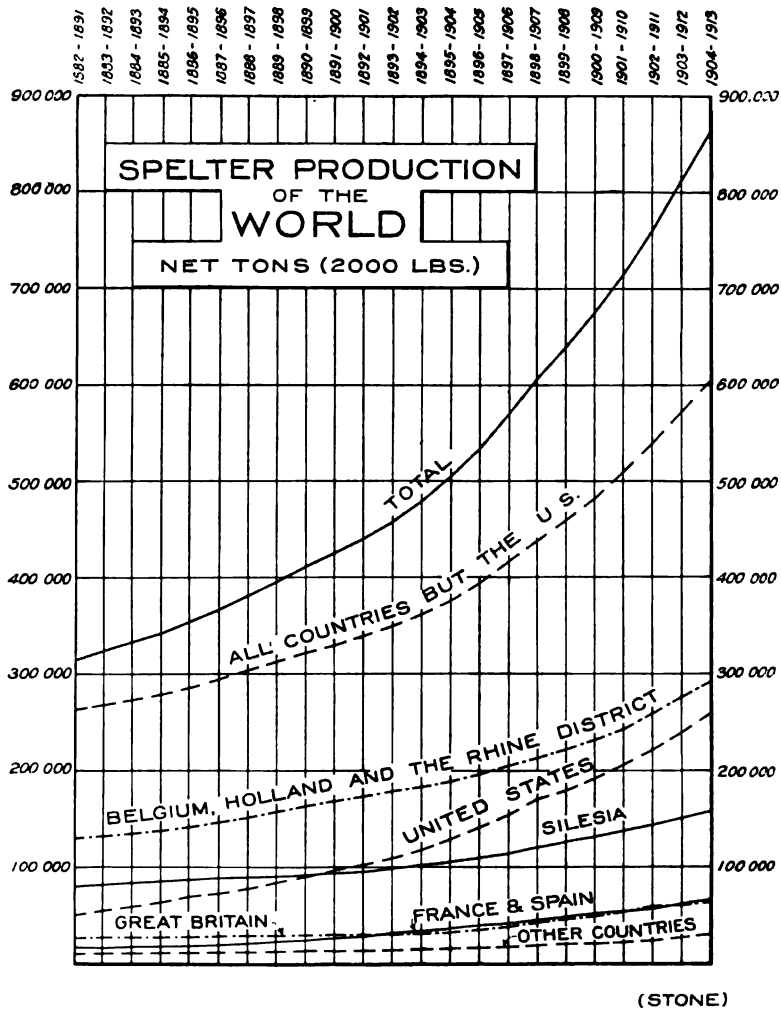
ores containing considerable amounts of lead, copper, gold or silver, in addition to zinc, that cannot be economically separated by mechanical means, the electric furnace may prove of advantage, and is likely to be of commercial value. The supply of such ores, however, is not nearly as large as is commonly supposed, and in a large proportion of cases they occur at points where cheap power is not available.



(STONE)

The accompanying diagrams show graphically the production of spelter for the United States and for the world. The diagram of the world's production gives in each case the average production for ten years, starting with 1884 to 1893, 1885 to 1894, etc. In this way, the extreme fluctuations are hidden and the general progress is shown. For the United States, it was impossible to make a similar diagram, as several districts were

not producing spelter for the entire time. In this, the output is therefore shown by years.



The following tables give the production of spelter in the United States and the world by districts, for periods of five years, in tons, with the percentage of the total and the increase or decrease in percentages of each period over the preceding:

TABLE I.

Spelter Production of the United States.

Net Tons (2000 lbs.)

	East and South	Mississippi Valley	Missouri and Kansas Coal Field	Kansas and Oklahoma Gas Field	Colorado	Pittsburgh District	Total
1884-1888.....	39,712	118,822	69,582	.....	....	.....	228,116
1889-1893.....	59,720	157,393	152,395	.....	....	.....	369,508
1894-1898.....	51,737	205,256	179,899	25,000	....	.....	461,892
1899-1903.....	50,148	253,519	90,973	314,388	877	.....	709,905
1904-1908.....	57,511	278,585	27,004	604,204	26,112	82,189	1,075,605
1909-1913.....	98,388	450,572	.....	755,395	37,637	161,253	1,503,245
Total	357,216	1,464,147	519,853	1,698,987	64,626	243,442	4,348,271
%	8.2	33.7	11.9	39.1	1.5	5.6	100.0
			Percentage of Make.				
1884-1888.....	17.4	52.1	30.5	...	..	...	....
1889-1893.....	16.2	42.6	41.2	...	..	...	100.0
1894-1898.....	11.2	44.4	39.0	5.4	..	...	100.0
1899-1903.....	7.3	35.5	12.8	44.3	0.1	...	100.0
1904-1908.....	5.4	25.9	2.5	56.2	2.4	7.6	100.0
1909-1913.....	6.5	30.0	...	50.3	2.5	10.7	100.0
			Percentage Increase Over Previous Period.				
1884-1888.....	...	...	....	...	....	...	....
1889-1893.....	50.4	32.5	119.0	...	....	...	62.0
1894-1898.....	—13.4	30.4	18.0	...	....	...	25.0
1899-1903.....	— 3.1	23.5	—49.4	1157.5	....	...	53.7
1904-1908.....	14.7	9.9	—70.3	92.2	2876.3	...	51.5
1909-1913.....	17.1	61.7	....	25.0	44.1	96.2	39.8

TABLE II.

Spelter Production of the World.

Net Tons (2000 lbs.)

	Belgium Holland and the Rhine	Silesia	Great Britain	France and Spain	Other Foreign	Total Foreign	United States	Total
1884-1888 ...	652,254	402,119	120,410	77,661	47,788	1,300,232	228,116	1,528,348
1889-1893 ...	705,028	438,108	148,046	92,632	53,406	1,437,220	369,508	1,806,728
1894-1898 ...	877,555	472,750	137,930	136,845	68,965	1,694,045	461,892	2,155,937
1899-1903 ...	952,760	537,795	174,625	184,320	75,280	1,924,780	709,905	2,634,685
1904-1908 ...	1,270,704	724,355	280,916	286,077	111,233	2,673,285	1,075,605	3,748,890
1909-1913 ...	1,661,568	854,666	337,046	355,678	184,471	3,393,429	1,503,245	4,896,674
Total ...	6,119,869	3,429,793	1,198,973	1,133,213	541,143	12,422,991	4,348,271	16,771,262
%	36.5	20.4	7.2	6.8	3.2	74.1	25.9	100.0
Percentage of Make.								
1884-1888 ...	42.7	26.3	7.9	5.1	3.1	85.1	14.9	100.0
1889-1893 ...	39.0	24.2	8.2	5.1	3.0	79.5	20.5	100.0
1894-1898 ...	40.7	21.9	6.4	6.4	3.2	78.6	21.4	100.0
1899-1903 ...	36.2	20.4	6.6	7.0	2.9	73.1	26.9	100.0
1904-1908 ...	33.9	19.3	7.5	7.6	3.0	71.3	28.7	100.0
1909-1913 ...	33.8	17.5	6.9	7.3	3.8	69.3	30.7	100.0
Percentage Increase Over Previous Period.								
1884-1888 ...	...	...	...	..	...	...	...	....
1889-1893 ...	8.0	8.9	23.0	19.3	18.8	10.5	62.0	18.2
1894-1898 ...	24.5	7.9	6.9	47.7	29.1	17.9	25.0	19.3
1899-1903 ...	8.5	13.8	26.6	34.7	9.2	13.6	53.7	22.2
1904-1908 ...	33.4	34.7	60.9	55.2	47.8	38.9	51.5	42.3
1909-1913 ...	30.8	18.0	20.0	24.3	65.8	26.9	39.8	30.6

DISCUSSION

Prof. Clevenger.

Prof. G. H. Clevenger,** Mem. A. I. M. E., felt that the author had discussed the hydrometallurgy of zinc much more briefly than its importance demanded. He stated that the principal difficulty involved in the operation of hydrometallurgical processes upon zinc ores has not been so much in getting the zinc into solution as in connection with precipitation. Fortunately the difficulties in connection with precipitation have recently been overcome in a very simple manner, so that at the present time there are four or five large companies producing electrolytic zinc successfully upon a semi-commercial scale, with a number of them contemplating large installations.

Professor Clevenger said that it is useless to suppose that hydrometallurgical processes are going to prove a panacea in connection with zinc. Also, he pointed out that ordinarily there is no trouble with high-grade ore, but that with low-grade ore, cost of fuel and refractories are the limiting conditions of the old methods of reduction. He added that in the course of time the hydrometallurgical processes would find their proper field.

Mr. Duschak.

Mr. L. H. Duschak,*** stated that excessively cheap power is not necessary for the successful electrolytic precipitation of zinc. At Palo Alto the Reed process has produced zinc at the rate of one pound of zinc per one-half kw-hr.

Mr. Bretherton.

Mr. S. E. Bretherton,* Mem. A. I. M. E., called attention to the necessity for having the zinc solution to be electrolyzed pure, and further stated that he was at that time devoting his attention to the treatment of flotation zinc concentrate by hydrometallurgical processes. He also called attention to the fact that the cost for power in Los Angeles would be less than one cent per pound, while at Anaconda it would be less than one-half cent per pound.

Mr. Carson.

Mr. G. C. Carson,† stated that zinc could be retorted for ½ cent per pound and that it cost two cents per pound to produce electrolytic zinc. He stated, however, that it is difficult to get retorts that will stand a temperature of 2000° F.

Mr. Dick.

Mr. J. C. Dick,‡ Mem. A. I. M. E., asked if the lack of suitable refractory clays has had anything to do with the non-production of spelter in the West.

Mr. Carson.

Mr. Carson stated that he thought it had not; that the primary reason is that people have not given the matter much attention. In England and Germany, Belgian clay is used.

** Stanford University, Calif.

*** San Francisco, Calif.

* San Francisco, Calif.

† San Francisco, Calif.

‡ Salt Lake City, Utah.

Mr. Beckman. **Mr. J. W. Beckman****** asked regarding the suitability of Stockton clay.

Mr. Carson. **Mr. Carson** replied that the clays used by him are selected by the pottery people, silica being mixed with the clay at the time of manufacture. He thought that the difficulty might be in connection with improper methods of manufacture.

Mr. Braden. **Mr. E. B. Braden,*** Mem. A. I. M. E., stated that more had been done in improving the metallurgy of zinc in the past year than had been done in the previous decade.

**** San Francisco, Calif.

* San Francisco, Calif.

Paper No. 192

ORE DRESSING.

By

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A historical sketch of the advancement of the science and art of ore dressing, dealing especially with the latest results, will cover, the author believes, the ground implied in a symposium.

As the subject is not well written up in its early development, the author will present it as, in his mind, it would have logically taken place.

The primitive metal worker picked out the rich specimens by hand and then smelted them. He next washed the ore pile to make the picking easier. He then noticed the small sizes of ore grains collecting in eddies and ripple marks, concentrated by the flowing of the water, and scraped these up. He then ran the mine fines through a trough and collected the small grains which were left behind. He now found that by putting in riffle blocks he could increase the catch. In this way, the wash trough for ore was developed, and finally, at a much later date, the riffle sluice for gold.

The next step in the evolution probably came by watching the waste flow away from the tail of the wash trough and build up a sand bank which was rich at the upper end and poor at the lower. From this, he constructed a second or lower trough, from which the building buddle was developed. He found that by sweeping transversely he could greatly aid in keeping the values at the upper end. This combination of a wash trough with riffle cleats and a building buddle is so efficient that it is today one of the most valuable prospector's tools, where the prospector is beyond the reach of modern mills and wants an approximate valuation of the concentrating qualities of the ore.

After getting the fixed building sweeping buddle (intermittent) he next made the Freiberg suspended building buddle (intermittent) with cam spring and bumping post. Then Ellenbecker invented his surface jerking table (continuous) at Calumet and the Gilpin County bumper came next in Colorado. Frue followed with his belt vanner, which is extensively used today.

While those improvements were in progress for two-mineral separation, Rittinger invented his continuous side-bump table with the bumping action at right angles to the flow of the water, separating the feed into several products according to weight and size. This was followed by the Wilfley table, which is one of the greatest advances ever made in ore dressing. It depends on the jerking progressive motion acting at right angles to the flow of the water and on the diagonal line of mechanical control of the separation.

The hand sieve for cleaning and hand picking, when used in a wash tub, must have very soon developed the principle of the jig, and next came the mechanical design for the hand jig with moving sieve. It was then arranged with a cam to be run by power. Some bright mind then said, "we are moving the sieve and letting the water stay still; why don't we move the water and let the sieve stay still?" and from that thought came the plunger jig. Then the jig was fed and discharged tailing continuously, the concentrate being skimmed off periodically and the hutch drawn off. Then the discharge for concentrate, with gate and dam, was introduced. This made the jig the entirely continuous machine which is in use today in the modern mills. Devices for softening the suction action, which tends to blind the screen, met with favor and have become part of the mill man's equipment. Among them are the sliding block, the Hodge jig, the crank arm, the Collom jig with spring, and the new Century jig with spring.

The Woodbury jig, by a combination of deep bed and gate and dam discharges at graded heights, combines jigging with removal of slime. The pulsator jig overcomes screen blinding entirely, and increases the capacity of a jig many times on account of the extremely soft bed it maintains. The Hancock jig of very large size—with moving screen divided off into com-

partments producing different grades of products, using little water and power, but with very large capacity, 400 tons or 500 tons in 24 hours, ranging in size from 8 mm. to 2 mm.—seems to be the climax in jigging at the present time.

In slime concentration, an early form of table is the Cornish frame, a plane surface, sloping from feed end to tail end, over which slime flows. Periodically, the feed is stopped and the concentrate flushed off. Following this came the convex, revolving, conical, round table which is a continuous-acting machine, feeding, washing, and discharging concentrate and tailing without stopping to discharge concentrate—a most useful table. The fixed blanket table for catching concentrate, and especially gold, was an early development.

In gold working, the canvas table, rectangular in form with a surface of cotton duck, run like a Cornish frame, has been much used. When fed with extremely fine slime, as in the Gates canvas plant, this is at its best, and is a very efficient machine. The Taylor Woodworth experiment at Lake Superior was intended to make the Gates system more automatic with less labor costs, flushing 25 tables, more or less, at once; but for various reasons it was discontinued. The most pronounced success, and the climax of the series, is the Anaconda rough surface, convex, conical, round table with very slow revolution and fed with extremely fine slime. This has accomplished more and better work than any of its predecessors.

FLOTATION PROCESS.

Devices depending upon surface tension, or as it is sometimes called, "greasy-flotation", are destined to play an extremely important part in the concentration of fine ores. They depend upon the great aversion that some minerals (metallic, sulphide and some ozides and carbonates) have to being wetted with water, which is increased by a film of oil on the mineral particle, while others have little or no aversion. The minerals which are difficult to wet with water are easily wetted with oil, even in the presence of water, while those that are easily wetted with water are not easily wetted with oil in presence of water. A little acid increases this differentiation in both directions.

If dry particles of pyrite and quartz 0.01 inch in size are lightly dropped on water, the pyrite particles will almost wholly float on the surface while the quartz particles will almost wholly sink, due in the first place to the surface tension, or aversion of the pyrite to be wetted, and in the second place, to the ease with which the quartz is wetted. If the quartz and pyrite are stirred violently with water and a very little oil, the oil is selective and attaches itself mainly to the pyrite and but little to the quartz; the presence of a little sulphuric acid increases the attraction of pyrite for oil, and the aversion of quartz for oil. If in any way small gas bubbles are introduced into the mass, they adhere to the pyrite, but not to the quartz. The bubbles act like life preservers and float the pyrite grains up to the surface. This scum or froth can be skimmed off, carrying with it the pyrite, and the quartz will be left behind.

There are many ways of getting the minute bubbles needed: carbon dioxide from the action of sulphuric acid on dolomite or siderite, sulphuretted hydrogen from blende or pyrrhotite and acid; air blown in in fine bubbles; vacuum fine bubbles of dissolved air to be drawn out of the water; air forced into water under pressure effervesces when pressure is removed; water as it begins to boil liberates fine bubbles of air. If oil is used in larger quantity, it floats up the sulphide by its buoyancy.

If quartz blende and galena are treated as above, the blende and galena will be found in the scum or froth; but if they be given a brief roast beforehand, the galena with slight coat of oxide will sink with the quartz and the blende will float in the scum. The galena can then be separated from the quartz by the concentrating tables.

If fine magnetic sand be mixed with the ore while the oil is being stirred in, the magnetite forms a catching nucleus for the ore, and the scum so formed can have the oil removed, to be used over again, and then the magnetite can be separated by magnet from the values.

PNEUMATIC PROCESSES.

The pneumatic riffle table (Sutton, Steele and Steele) avoids the use of water in concentrating ores where water is scarce.

The Plumb air jig is proving a valuable helper in separating certain concentrate products where the wet machines do not give perfect enough separation, for example, blende from galena.

THE MAGNET.

There are three leading conditions, and consequent processes, whereby the magnet may be used for separating the mineral grains that are attracted from those that are not: (a) minerals that are strongly magnetic, (b) minerals that are weakly magnetic, and (c) minerals that are not magnetic but may become so by suitable treatment.

(a) Strongly-magnetic minerals may be separated from others, whether or not of the same specific gravity. Many magnetic machines have been devised; perhaps none has more capacity or is more efficient than the Ball-Norton belt machine. This, by its numerous magnetic poles of alternate polarity—the earlier of stronger magnetic force, the latter of weaker—will separate, first, a tailing of no commercial value, next, a middling for re-crushing and re-treatment and, finally, a concentrate for the furnaces. This concentrate is made especially free from the non-magnetic minerals owing to the alternate polarity of the poles, which causes the tufts of mineral grains to be inverted with every new pole, and thus the less magnetic or non-magnetic grains are sifted out from their entanglements.

(b) For weakly-magnetic minerals, a number of high-power magnetic machines have been devised, among them perhaps none has more efficiency than the Rowand-Wetherill magnet. These magnets can separate minerals that have so little magnetic susceptibility that they show none of it to a strong, permanent hand magnet. For example, limonite may be completely separated from quartz. Again, monozite may be completely separated from garnet and hypersthene (more magnetic minerals) and from zircon and quartz (less magnetic minerals).

Differential Magnetic Work on Weakly Magnetic Minerals.

A little 6-inch Wetherill magnet (Rowand type) at Portland, Oregon, separated black sand by repeating the treatment each time with increased amperage, the minerals taken out

were as follows: With 0.2-amperes electric current the magnetite was taken out; 1.1 amperes took out the ilmenite; 1.6 amperes, the chromite and platinum; 1.75 amperes, the garnet; 2.2 amperes, the hypersthene and olivene; 3.5 amperes, the monazite; leaving zircon and quartz, gold and iridium as non-magnetic.

(c) The separation of dark-colored blende from pyrite is generally in class (b), the blende being the weakly-magnetic mineral, but with resinous, light-colored blende (commercially non-magnetic), the process is more complicated. The pyrite is coated on its surface with a thin film of magnetite or pyrrhotite by a brief oxidizing roast; the product so prepared easily yields to the treatment described in class (a). A 1 mm. grain of pyrite exposed between one and two minutes to oxidation at a red heat reaches maximum magnetic properties; with longer time or shorter time, it has less magnetism.

In separating siderite from resinous blende, the procedure is as with light-colored (non-magnetic) blende, where the roasted siderite is the magnetic mineral only. The exposure required in the furnace is to a higher heat and for a longer time than with pyrite.

STATIC ELECTRIC SEPARATION.

Static electricity from a frictional machine effects a separation on certain minerals of the same, or nearly the same, specific gravity. If a conductor, for example, a brass cylinder, is charged with one pole of a static machine and grains of sand of mixed minerals are dropped on to it, the good conductors will at first stick tight to the cylinder, but as soon as fully charged, will fly off into space. The poorer conductors do the same, but it takes them a longer time. The current from a dynamo will do the same, provided its voltage is sufficiently high. By adjusting the currents rightly, static electricity can give three products: (1) very good conductors, which fly off immediately; (2) middling conductors, which do not get sufficiently charged, and so stick to the pole (they have to be brushed off the pole); and (3) the very poor conductors, which simply tumble off the cylinder as it slowly revolves.

BREAKING.

Very early in the scheme of concentration the use of the hand hammer for cleaning the values from the waste came in. This was followed later by hammers driven by power, or crude stamps. These were gradually developed until the California stamp was evolved.

Gravity stamps are common, weighing 1000 lbs. to 1200 lbs. or even 2000 lbs., crushing down to ¼ inch maximum and to 1/30 inch minimum. A recent design has a cam with uniformly accelerated motion which saves some power and most of the noise.

The rock breakers of the Blake type were introduced to do away with the heavy work of coarse breaking by hand.

Rock breakers of the Blake type are standard for milling work. They are made up to 24 inches by 36 inches jaw opening. One firm makes one much larger than that—66 by 76 inches jaw opening. The 76-inch machine breaks to 12 inches; the 36-inch machine to 4 inches, the smallest to 1½ inches in size.

The Dodge breaker is used in places where a constant maximum limit in size is especially important. They break down to 2 inches or even 1 inch.

The Gates and McCully spindle breakers are used to take the run of mine and bring it down to some uniform maximum size; 4-inch size is common for the large machines. The smaller machines crush to 2 inches or 1½ inches.

Rolls are standard for intermediate breakers. They are made as large as 54 inches by 18 inches for the greatest capacity and efficiency. Belted rolls are much more common than geared rolls. They break to a maximum of about 1 inch and to a minimum of about 1/16 inch. The Symons disc crusher breaks from 2 inches to ¼ inch with great capacity.

Chile mills and tube mills, cylindrical or conical, are prominent machines for fine crushing preparatory to concentration. Their breaking limits range from 1/16 inch, or 1½ mm., maximum down to 1/50 inch, or ½ mm. minimum size; tube mills are universal for the finer sizes. In some cases, the tube mills are required to break much finer. The finest limit may be 0.08 mm., or 3/1000 inch.

Steam stamps weigh up to 2¾ tons and usually crush conglomerate at the rate of 300 tons per 24 hours from 3-inch down to 3/16-inch, and amygdaloid at the rate of 600 tons per 24 hours, from 3-inch down to ⅝-inch.

IMPROVEMENTS IN MILLING.

In the Lake Superior Copper regions, the improvements that have done the most to reduce waste and increase yield are: (1) the mortar discharge, which removes copper nuggets from the steam-stamp mortar almost as soon as they are freed from rock. Formerly these nuggets remained in the mortar and were abraded, yielding much fine copper slime—too fine to be saved. (2) The use of a coarse stamp discharge screen, ⅝-inch round hole and a trammel ¼-inch hole, giving a chance to catch ⅝-inch to ¼-inch nuggets on an outside jig or hydraulic classifier and saving much sliming of copper. The ⅝- to ¼-inch jig tailing is re-crushed and put back into the system. (3) The re-crushing and washing of all coarse tailing for the recovery of included grains of copper.

At Anaconda, Montana, the latest flow sheet shows that the rock will be crushed primarily to 7 mm. and then screened on a 1½ mm. screen; the oversize yields concentrate on Hancock Jig and the middling is re-crushed to 1½ mm. The primary and re-crushed (1½ mm. to 0) materials go to an Anaconda classifier, yielding slime (.08 to 0 mm.) for flotation and sand for Wilfley tables. The middling from these (no tailing is made) goes to tube mills and Anaconda classifiers, making slime (.08 to 0 mm.) for flotation and the sand returns to the tube mills. The primary flotation will yield two products, low grade concentrate and tailing with .08% copper. The primary concentrate will go to secondary flotation and yield high grade concentrate and middling. This last will go back over again to the primary flotation. The yield of a final tailing with only 0.08% copper is a most extraordinary achievement.

The improvements in Missouri Lead, Idaho Lead and Arizona Copper are along the same general lines as Montana, namely, jigs for coarse sands, classifiers and tables for finer sands, and flotation for the slime. The limit at which re-crushing stops is much coarser in the lead and silver-lead mills than

in the copper mills, owing to the lower value of the chief metal value.

The importance of classification preparatory to Wilfley-table work seems to be everywhere admitted; by it the fine free mineral losses in Wilfley-table tailing are mostly prevented.

The porphyry coppers of Utah and Arizona generally use a roughing riffle table; the tailing from this goes to classifiers and the various products to vanners—the corrugated belt for the coarser sizes and the smooth belt for the finer. Flotation has been taken up and is to increase the saving on the older method very greatly. The wonderful success of the porphyry copper mines seems to have been due to the insistence on enormous capacity, even if high saving was not at first attained. Now the high saving is coming through the flotation process.

The Timber Butte mill of Butte, Montana, gives a very good example of the most advanced methods used on complex ore, combining water concentration and flotation. The ore, carrying zinc, lead, copper, gold and silver, is crushed to 2½ mm. Roughing tables then give (1) mixed minerals, (2) coarse zinc and (3) slime. The mixed minerals (1) by classifiers, jigs and tables give (A) lead, (B) mixed minerals and (C) coarse zinc. The mixed minerals (B) are re-crushed to 20 mesh (probably ¾ mm.), then classifiers, and tables give (a) lead, (b) mixed minerals, (c) coarse zinc, and (d) slime. The mixed minerals (b) are re-crushed to 60 mesh (probably ¼ mm.), and all the slime added to them. Flotation separates the (1) zinc and lead from the silica and insolubles. Then wet concentration upon the flotation zinc and lead gives (1) lead and (2) fine zinc, yielding a high extraction of zinc, lead and copper. The silver and gold are distributed in with these other metals.

DISCUSSION

Mr. Bretherton.

Mr. S. E. Bretherton,* Mem. A. I. M. E., asked if barite, calcite and other gangue minerals like quartz would be rejected by flotation.

Prof. Richards.

Prof. R. H. Richards,** Hon. Mem. A. I. M. E., replied that generally it was only the sulphides that were carried to the surface in flotation, but that there might be exceptions to this general statement.

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Mr. Carson. **Mr. G. C. Carson***** asked regarding the behavior of zinc carbonate in flotation.

Mr. Parmelee. **Mr. H. C. Parmelee****** replied that some work had been done along this line by students at the Colorado School of Mines, but his impression was that the results were negative.

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Paper No. 193

ELECTROMETALLURGY.

By

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Electrometallurgy is not a separate branch of metallurgy, like smelting or refining, nor is it restricted to any metal or any class of metals, but it is rather a collection of methods which may be employed to a greater or smaller degree in any branch of the metallurgy of any metal, and the common characteristic feature of all these methods is that they make use of some property of the electric current. A logical classification of the whole of electrometallurgy must be based on the specific properties of electricity which are utilized for metallurgical ends.

Any property or effect of the electric current may be employed usefully in metallurgy. Thus the magnetic effect is utilized in electromagnetic separation; the difference in electric conductivity of different materials in electrostatic separation; the old familiar phenomenon of the "electric wind" in the Cottrell process of electrostatic dust precipitation, and so on. But in the field commonly called electrometallurgy—and to this field the present summary is restricted—two different fundamental properties of the electric current are employed: first, its heating effect; second, its electrolytic effect. If the heating effect alone is utilized, we speak of electric furnace processes; if the electrolytic effect is utilized, we speak of electrolytic processes. If both the heating and the electrolytic effects are utilized, we speak of electrolytic furnace processes.

I. ELECTRIC FURNACE PROCESSES.

A. Fundamental Principles.

There is no specific electrical feature which distinguishes an electric-furnace reaction as a chemical reaction from those taking

place in ordinary metallurgical processes. The distinguishing feature rests in the apparatus, the heat required for the reaction being produced electrically. If the same amount of heat would be generated in the same material in some other way than by electricity (all other conditions being equal), the reactions would be exactly the same. At least, this statement is true for all electric-furnace processes at present in commercial use in electro-metallurgy.

Compared with the production of heat from fuel, electrical heat has two advantages: First, a considerably higher temperature may be obtained; this is limited in arc furnaces by the temperature of the arc, which is around 3400 deg. C. (or around 6200 deg. F.), and in resistance furnaces chiefly by structural considerations, such as the availability of insulating refractories, etc. While in ordinary metallurgical furnaces temperatures up to 2000 deg. C. are obtainable, temperatures up to 3400 deg. C. can be produced without special difficulty in the electric furnace. Secondly, for reactions requiring certain refinements, the electric furnace has the advantage of permitting easier control of the conditions of operation, such as temperature, chemical nature of the atmosphere, etc.

On the other hand, the disadvantage of electrical heat, as compared with heat from fuel, is its much higher cost under all ordinary normal conditions. To figure the cost of electrical heat, we have the fundamental conversion factors:

1 kilowatt-hour = 860 kilogram-calories.
1 kilogram-calorie = 0.001163 kilowatt-hour.

One kilowatt-hour is equivalent to 860 kg.-calories, or about the full heat which can be produced from 0.1 kg. of good coal when completely burnt to CO_2. If the cost of one ton (2000 lbs. = 907 kg.) of coal is a dollars and if the efficiency of heat production by burning coal is m percent, then the cost of producing 860 kg.-calories from burning $10/m$ kg. coal, is $a/(90.7\ m)$ dollars. On the other hand, if the cost of 1 kilowatt hour is b cents and if the efficiency of producing heat from electrical energy is n percent, the cost of 860 kg.-calories from $100/n$ kilowatt hours is $b\ n$ dollars. Hence electrical heat will be cheaper than heat produced by combustion of fuel if $a\ n$ is greater than $90.7\ b\ m$.

If we assume efficiency figures which are not unfair under practical conditions, namely, an efficiency $m = 25$ percent for fuel heating and an efficiency $n = 75$ percent for electric heating, then electric heat is cheaper than fuel heat if a is larger than 30.2 b, i. e., if the cost of one ton of coal in dollars is more than 30.2 times greater than the cost of 1 kw.-hr. in cents. For instance, to compete with coal at \$6 per ton, the electrical kilowatt-hour would have to cost less than 0.2 cent. This shows that were it not for its other important features, electric heat could not compete with fuel heat under ordinary conditions.

If we have an electric-furnace process which will work continuously with full load all year, then the cost of the electric horsepower-year will be 65.7 b dollars; hence, electric heat will be cheaper than fuel heat if the cost of one ton of coal in dollars is more than 30.2 ÷ 65.7, or, say, one-half the cost of the electric horsepower-year. This is apparently a more favorable view of the situation, especially in neighborhoods where fuel is expensive and hydro-electric power is really cheap (say below \$10 per electric horsepower-year). But unless absolute continuity of the process is assured, it is safer to base such calculations on the cost of the kilowatt-hour instead of the horsepower-year.

The result of this calculation is well illustrated by electrochemical geography. The chief centres of electrochemical activity, where electric heating is employed at a large rate, are Niagara Falls in this country, the West Coast of Norway, with its abundant waterfalls, and the waterfall districts of France. That electrochemical methods are able to rearrange the industrial geography of the world is illustrated by the example of Norway.

B. Classification of Electric Furnaces.

The electrical energy is changed into heat either by producing an electric arc and thereby generating heat, or by the Joulean effect, the electric energy being changed into heat on account of the electric resistance of the path of the current, the rate of heat produced being $I^2 R$ watts or 0.24 $I^2 R$ gram-calories per second, if I is amperes (effective amperes in case of alternating current) and R is ohms (resistance, not impedance). Accordingly, electric furnaces are divided into arc furnaces and

resistance furnaces. In a resistance furnace, the material in which the electric energy is changed into heat is called the resistor. In many cases it is difficult to say whether a furnace belongs to one or the other class, since both effects may be superposed.

Arc furnaces are subdivided into direct and indirect arc furnaces. In a "direct arc furnace" one or several arcs play between the end or ends of the electrodes and the charge (Siemens, Heroult, Girod, Keller, Groenwall, Nathusius, Rennerfelt, de Laval, Johnson, and others). In some of these types there are also additional electrodes (or terminals) provided in the sides or in the bottom of the furnace. In the "indirect arc furnace" arcs play between the ends of the electrodes above the charge and heat the charge below by radiation, there being no arcs between the electrodes and the charge itself (Stassano).

Resistance furnaces may be subdivided according to the nature of the resistor, whether the electric heat is produced in the charge itself or in a special resistor, in contact with the charge (silicon furnace of Tone) or not in contact with the charge (zinc furnace of FitzGerald and Thompson). Resistance furnaces in which the electric heat is produced in the charge itself may be subdivided according to the method of introducing the electrical energy into the charge, whether this is done through terminals or electrodes (Hering and others) or by electromagnetic induction, as in the induction furnace (Colby, Kjellin, Gin, Frick). In the Roechling-Rodenhauser combination furnace, there is a superposition of two heating effects, first, by induction and, second, by an auxiliary secondary circuit, the ends of which are connected to metallic "pole plates" embedded in the furnace walls.

Any of these different types has its special advantages and disadvantages, and the selection of a furnace type depends to a large extent on the conditions of the industrial problem. Direct current and alternating current may both be used for operation of an electric furnace, but alternating current has two very important advantages: first, electrolytic effects, which are not desired in pure electric-furnace reactions, are excluded; second, alternating current permits easier regulation. The induction furnace always requires alternating current.

C. Metallurgical Applications of the Electric Furnace.[1]

Aside from smaller special applications of the electric furnace, such as the heating of bars and billets (Baily), there are two chief applications of the electric furnace in the metallurgy of different metals; first, for melting and refining; and second, for reduction processes.

1. Melting and Refining. While there appears to be a promising field for an electric brass furnace, the principal application of the electric furnace for melting and refining has been in the past in connection with the steel industry,[2] in which the electric furnace has been developed in three different directions:

(1). For the production of high-grade steels of crucible-steel quality, in competition with the crucible furnace. In this field the electric furnace is firmly established and steadily progressing. It has the advantage of larger units and smaller expenses for repairs and wages, while the product of the electric furnace is as good as that of the crucible-steel process and it is not necessary to use as pure and expensive starting materials. For steel refining in the electric furnace, the possibility of producing a higher temperature in the slag is important (because it permits the use of more basic, yet still fluid, slags), but of greater importance is the neutral or reducing atmosphere, since it permits chemical reactions which are impossible in oxidizing furnaces, such as removal of sulphur as calcium sulphide and removal of phosphorus as phosphide.

It seems only a question of time when the electric furnace will obtain commercial supremacy in the production of high-grade steels. The figures for 1914 for Germany and Austria, where this evolution has probably proceeded furthest, are suggestive. The total amount of crucible steel and electric steel produced in Germany, in 1914, was 184,432 tons, of which 95,096 tons, or 51.6 percent, was crucible steel and 89,336 tons, or 48.4 percent, electric steel. Electric steel has, therefore, now reached practically the same importance as crucible steel in Germany. The total amount of crucible steel and electric steel made in Austria-Hungary, in 1914, was 37,401 tons, of which 19,844 tons, or 53.1 percent, was electric steel and 17,557 tons or 46.9

percent was crucible steel. That is, Austria-Hungary now produces more electric steel than crucible steel.

(2). The electric refining of molten steel from the Bessemer converter or from the open-hearth furnace for the production of steel for large-tonnage products of better than present normal quality (structural steels, steel for rails, etc.) has been studied on a large scale especially by the United States Steel Corporation. If successful, this would be the biggest application of the electric furnace in the steel industry, and the combination of the electric refining furnace with the Bessemer converter would mean a revival of Bessemer converter activity. But the electric refining cost is still considered prohibitive for most large-tonnage products, although it is quite likely that further metallurgical progress will result in the needed reduction of costs. If only the cost of combined converter and electric-furnace treatment on a large scale can be brought down to present open-hearth treatment cost, it would be a great industrial advance.

(3). A third application of the electric steel furnace is in the steel foundry for making castings, especially automobile castings. In this field the electric furnace is steadily gaining favor at present. (See the A. I. M. E. paper by Kranz, San Francisco meeting, 1915).

A great many figures on specific energy consumption in kilowatt-hours per ton of steel have been published, but they are not easily comparable, since the specific energy consumption depends on the size of the furnace, the condition of the raw material (especially whether liquid or cold), and the degree of refining desired. The following figures for Heroult furnaces will give, however, a general idea of the amount of energy required.

Size of Furnace and Rating	Molten Steel	Cold Scrap
One-ton (250 kw.)	400 kw.-hr.	1000 kw.-hr.
Three-ton (400 kw.)	250 to 300 kw.-hr.	800 kw.-hr.
Five-ton (700 kw.)	180 kw.-hr.	700 kw.-hr.
Fifteen-ton (2000 kw.)	150 kw.-hr.	Less than 700

A special application of the electric melting furnace in the steel industry is the melting of ferromanganese, since the addition of molten instead of solid ferromanganese to steel means a distinct saving of alloy and better deoxidation. (Metallurgical

and Chemical Engineering, Volume 12, page 295; also the recent German monograph by Rodenhauser on this subject.)

2. Reduction Processes. If the electric furnace is used for the reduction of metals from compounds, the distinction from the fuel-heated reduction furnace is that electrical energy instead of fuel is used for heating the furnace charge, but the same amount of reducing agent (carbon or some other suitable element, for instance, aluminium) is required in the electric furnace as in the fuel-heated furnace, since nothing of an essential nature is changed in the chemical reaction.

The first metallurgical application of the electric furnace in this field has been in the reduction of highly refractory compounds requiring an unusually high treatment temperature. Thus, for the production of silicon-copper, A. H. Cowles treats a mixture of copper, silica, and carbon in an electric furnace, reducing the silica by means of carbon and obtaining an alloy of copper and silicon, which is used in copper foundries for deoxidizing purposes.

On exactly the same principle is based the production of ferro-alloys in the electric furnace. For making ferrosilicon, the charge consists of iron, silica, and carbon. Instead of iron, iron oxide may be used in the charge, but then it is necessary to use more carbon, and the power consumption is also higher. According to Keeney, when iron turnings are used in the charge, the specific energy consumption of a modern ferrosilicon furnace of 750 kw. or more capacity is 6000 to 8000 kw.-hr. per ton of 50 percent ferrosilicon, and about 3500 to 4000 kw.-hr. for the 25 to 30 percent grade. Using iron ore instead of iron turnings, one company made 28 percent ferrosilicon with a specific energy consumption of 5930 kw.-hr. per ton.

The electric furnace is indispensable at present for the production of rich grades, low in carbon, of various ferro-alloys, especially ferrochromium, ferrotungsten, ferromolybdenum, high-percentage ferrosilicon, etc. The chief seat of this important industry is Savoy, France, but plants making ferro-alloys are distributed over many countries where cheap hydro-electric power is available. The foundation of the present ferro-alloy industry resulted originally from an industrial crisis of the calcium carbide industry in Europe, when many electric-furnace

plants for carbide manufacture were compelled to shut down or make something else instead of carbide.

In connection with ferrosilicon, the manufacture of metallic silicon by the process of F. J. Tone must be mentioned, in which the reaction $SiO + 2C = Si + 2CO$ is employed. It is used not only in the steel industry (in place of ferrosilicon), but metallic silicon castings have many applications in the chemical industries on account of their non-corrosive qualities. It is interesting to reflect that while silicon is one of the most abundant elements on earth in form of compounds, it has not been commercially available in elemental form until its reduction at a moderate cost became possible through the electric furnace.

The production of metallic tungsten, molybdenum and other more or less rare metals in the electric furnace should be mentioned in this connection, because the use of the electric furnace in their case is due to the same technical and commercial reasons as in the cases just considered.

The situation is very different with the reduction of iron[3] in the electric furnace, which is commercially successful in Scandinavia and which has also been tried on a commercial scale in Heroult, Shasta County, California. The best result which has been obtained in Scandinavia, in actual operation, with respect to specific energy consumption is 5 tons per kw.-year. This figure emphasizes the importance of very low cost of electrical energy as compared with coke. According to Harbord, when electrical energy is available at $10 per electric horsepower-year and coke costs $7 per ton, the cost of production of pig iron in the electric furnace is approximately the same as the cost of producing it in a modern blast furnace.

On the other hand, the electric furnace has distinct advantages. Ores can be treated in it which could not be economically worked in the past. Ores of high-sulphur content can be made into pig iron containing only a few thousandths of a percent of sulphur. Titaniferous iron ores containing up to 5 percent can be successfully treated. The silicon content can be varied as required for the class of pig to be produced. For carbon as reducing agent it is not necessary nor advisable to employ coke, since charcoal and peat-coke can be satisfactorily used. Perhaps the most promising feature of the reduction of iron in the

electric shaft furnace is the possibility[4] of producing "pig steel" directly from iron ore. This is a metal with 2.2, or less, percent of carbon, a very small amount of silicon and manganese, low in sulphur and phosphorus. It can be refined to steel at a considerably lower cost than ordinary pig iron.

Finally, zinc[5] must be mentioned as offering considerable possibilities for the application of electric reduction processes. The advantages would be in the reduction of operating cost which would follow in various directions from the successful substitution of the large-size electric furnace for the small present retort, and also in the possibility of treating certain complex ores which cannot be treated economically at present. Zinc has been made commercially in the electric furnace by the process of C. G. P. de Laval. The chief obstacle in the commercial development of electric zinc smelting has been the difficulty of condensing the zinc vapor into liquid spelter, as almost all early experimenters have been troubled with the production of an excessive amount of blue powder; but this trouble seems now to have been overcome to a large extent (especially by W. McA. Johnson, as well as by FitzGerald and Thompson). Most electric zinc furnaces use carbon as reducing agent, the ore being previously roasted and pre-heated. The electric furnace reaction is $ZnO + C = Zn + CO$. In the Imbert process, zinc sulphide is reduced by iron as reducing agent, the reaction being $ZnS + Fe = Zn + FeS$.

II. ELECTROLYTIC PROCESSES.

A. Fundamental Principles.

The fundamental feature of electrolytic processes producing metals from their compounds is that the electric current directly decomposes the compound, yielding the desired metal without any other reducing agent being required. For instance, in the production of copper from compounds found in nature, the usual metallurgical procedure is to change the natural compound by roasting into oxide and reduce the oxide into metallic copper in a fuel-heated furnace by means of carbon as reducing agent. On the other hand, the procedure in a process using electrolysis would be to change the natural copper compound into

a water-soluble compound (sulphate or chloride, etc), dissolve in water, and electrolyze, whereby metallic copper is directly deposited on the cathodes.

The change into a water-soluble compound in this procedure is necessary, because to be decomposed by electrolysis the compound must be in the form of an "electrolyte" and the two classes of electrolytes for industrial applications are, first, solutions (especially solutions in water), and, second, fused salts. (The electrolysis of fused salts will be discussed under Electrolytic-Furnace Processes.)

The fundamental law of electrolysis is Faraday's law, which gives the exact relation between the weight of the products of electrolysis and the quantity of electricity (in coulombs or ampere-seconds) passing during electrolysis. In almost all important metallurgical processes using electrolysis, the desired metal is deposited on the cathode out of the metallic compound forming the electrolyte, and Faraday's law may be stated for this case as follows:

If nothing but the desired deposition of the desired metal happens at the cathode (that is, no simultaneous liberation of hydrogen gas, no simultaneous deposition of other non-desired metals, nor any other "secondary" reaction), then if n is the valency of the compound from which the metal is deposited, the deposition of one gram-atom of the metal on the cathode requires the passage of $96{,}540 \times n$ coulombs. For instance, in the case of copper (atomic weight 63.6) the deposition of one gram-atom or 63.6 grams of copper requires 96,540 coulombs in case of a mono-valent copper salt solution (like cuprous chloride), but $2 \times 96{,}540 = 193{,}080$ coulombs in case of a bi-valent copper salt solution (like cupric sulphate). In the latter case it will make no difference how the passage of 193,080 coulombs or ampere-seconds takes place (whether 193,080 amperes pass for one second or 96,540 coulombs for 2 seconds or 64,360 coulombs for 3 seconds, etc.), as long as the fundamental assumption placed at the beginning of this paragraph is fulfilled, namely, that nothing but the desired deposition of copper from the given electrolyte happens at the cathode. If, however, a new reaction, like liberation of hydrogen, is started, for instance

by raising the voltage, less copper will be deposited, and the amount of copper actually deposited in percent of the theoretical amount following from Faraday's law is called the "ampere-hour efficiency" of the process.

The metal deposited on the cathode is the cation. What happens simultaneously at the anode depends on the nature of the anion, and the latter also determines, to a certain extent, the valency.

Typical mono-valent anions are Cl, Fl, OH, ClO_3, etc. Typical bi-valent anions are SO_4, SiO_3, CO_3, C_2O_4, CrO_4, etc.

Of cations, hydrogen, sodium, potassium, lithium, and silver are mono-valent; zinc, barium, calcium, cadmium, cobalt, magnesium, and lead in usual or plumbic salts are bi-valent. Copper is mono-valent in cuprous compounds and bi-valent in cupric compounds. Mercury is mono-valent in mercurous salts and bi-valent in mercuric salts. Iron is bi-valent in ferrous salts and tri-valent in ferric salts. Manganese is bi-valent in manganous salts and tri-valent in manganic salts. Nickel is bi-valent in nickelous salts and tri-valent in nickelic salts. Tin is bi-valent in stannous salts and tetra-valent in stannic salts, etc.

The cost of the electrical energy consumed in an electrolytic process depends directly on the watt-hours consumed, but the weight of metal deposited depends on the ampere-hours. Hence, as watt-hours = volts $\times$ ampere-hours, the old saying is that in an electrolytic process amperes bring money and volts cost money.

While the voltage should, therefore, be reduced as much as possible, there is for every electrolytic reaction a minimum voltage below which it is impossible to go if the reaction is to proceed. In the case of any electrolytic cell through which an electric current is passed from the outside, the equation of the principle of conservation of energy states that the electrical energy is partly changed into Joulean heat, $I^2R \times$ time, due to the internal resistance R of the cell, and partly into the chemical energy, required for the chemical process in the cell. The equivalent voltage equation states that the voltage impressed upon the terminals of an electrolytic cell is the sum of the voltage drop $I\,R$ (due to the internal resistance R of the cell) and the e.m.f. of the

reaction proper. The voltage drop $I R$ is a plain loss* and should be made as small as practicable. The e.m.f. proper of the chemical reaction in the cell is given exactly by the Gibbs-Helmholtz equation

$$e = 0.0000434 \frac{W}{n} + \frac{T de}{dT}$$

where e is the e.m.f. in volts, required to be impressed on the terminals of the cell for the electrometallurgical process to go on, W the total energy of reaction in gram-calories per gram-atom of metal deposited (W being figured as positive, if energy must be supplied from the outside for the reaction to go on) n the valency of the deposited metal in the electrolyte, T the temperature in absolute degrees and $\frac{de}{dT}$ the temperature coefficient of the e.m.f. at the temperature T.

For most practical purposes it is permissible to neglect the second item on the right hand of our last equation. We have then simply Thomson's rule:

$$e = 0.0000434 \frac{W}{n}$$

B. Classification of Electrolytic Processes.

Energy considerations of this kind are the basis of the old and important classification of electrolytic processes into such with soluble and insoluble anodes. In the most important processes using soluble anodes (electrolytic refining, electroplating, etc.), practically the same weight of metal is dissolved from the anode as is deposited on the cathode, so that the energy set free by anodic solution and the energy consumed by cathodic deposition balance each other and the total reaction energy is zero, hence the e.m.f. proper is also zero. Therefore, in electrolytic refining and electroplating, the voltage impressed is practically wholly consumed by the internal resistance.

On the other hand, in processes using non-soluble anodes, the reaction energies at the anode and at the cathode do no

* We deal in this chapter only with straight electrolytic processes in which the electric current is not intentionally used for electric heating. If in such processes it is desired to heat the electrolyte to a higher temperature, as, for instance, in electrolytic copper refining, some method of fuel-heating is employed, being more economical. The processes requiring internal electric heating will be treated separately in chapter III under Electrolytic Furnaces.

longer balance each other, hence the total reaction energy and the e.m.f. of the reaction are not zero, but can be calculated from thermo-chemical data. For instance, in the old Siemens-Halske process for winning copper from sulphate solutions, the final step is cathodic deposition of the copper from copper sulphate solution, with simultaneous oxidation of ferrous sulphate to ferric sulphate at an inert carbon anode:

$$Cu\,SO_4 + 2\,Fe\,SO_4 = Cu + Fe_2\,(SO_4)_3.$$

To find the energy of reaction, we have the following data (Richards, "Metallurgical Calculations", vol. I, pp. 24 and 25):

$$Cu + S + 4\,O = Cu\,SO_4 + 197{,}500$$
$$2\,Fe + 2\,S + 8\,O = 2\,Fe\,SO_4 + 469{,}800$$
$$2\,Fe + 3\,S + 12\,O = Fe_2\,(SO_4)_3 + 650{,}500$$

By substracting the sum of the first two equations from the third equation we get

$$Cu\,SO_4 + 2\,Fe\,SO_4 = Cu + Fe_2\,(SO_4)_3 - 16{,}800.$$

Hence in order to let this reaction go on from the left to the right hand in the equation, if each symbol of an element means a gram-atom, energy in the amount of 16,800 gram-calories must be furnished. Therefore, in the formula of Thomson's rule

$$e = 0.0000434\,\frac{W}{n}$$

we have $W = +\,16{,}800$ and $n = 2$, because Cu is bi-valent in $Cu\,SO_4$, hence

$$e = 0.36 \text{ volt.}$$

This is the theoretical e.m.f. of the reaction. The total voltage which must be impressed on the terminals of the cell equals 0.36 volt plus the voltage required to overcome the resistance of the cell.

C. Metallurgical Application of Electrolytic Processes.[6]

1. Electrolysis with Soluble Anodes—Electrolytic Refining of Metals. The distinction between processes with soluble and insoluble anodes may be expressed in a somewhat different way. Electrolytic processes with soluble anodes represent a finishing reaction. The metal under treatment must already have been brought into a rather high state of purity. The power consumption is then relatively low and the danger of the solutions becoming fouled by accumulation of impurities is reduced;

for it is a fundamental principle of any electrolytic operation that the conditions of the system shall remain unchanged during operation.

Electroplating[7] and electrotyping[8] are somewhat outside of the scope of what is now understood to be the field of electro-metallurgy. The discussion in this chapter is therefore restricted to the electrolytic refining of metals.

In the electrolytic refining of metals, the starting material is a highly concentrated alloy, and the object is to remove the last impurities and to recover not only the principal metal in pure form, but also the foreign metals, especially the precious metals. The impure metal (alloy) is made the anode, and the fundamental principle of the process is that by the electrolytic action the metal to be refined is dissolved from the anode, passes into the electrolyte, and is deposited from the electrolyte on to the cathode in pure form. The foreign elements (impurities) are intended to remain back in the anode or in the anode slime without being dissolved, or if they are dissolved in the electrolyte, they are intended to remain in solution without being deposited on the cathode, on the principle that their deposition would require a higher minimum voltage than the voltage which is used in the process and which is sufficient for the deposition of the metal which is being refined. Since there are usually quite a number of different elements present as impurities, the apparently so simple process of electrolytic refining of metals becomes exceedingly complicated, especially in view of the additional separate problems of separating and winning the precious metals from the anode slime or from the solution. On the degree to which these different problems can be solved, depends the industrial success of the refining process.

Copper Refining.—This most important of all electrolytic refining processes is being treated in detail in two papers before this Congress, by Lawrence Addicks and A. C. Clark, respectively, so that we need not deal with it at this place.

Silver Refining.—The principal commercial problem of silver refining relates to the treatment of the bullion produced by copper refineries, to recover the silver and gold. This bullion may be treated either with the old sulphuric acid parting proc-

ess or electrolytically by the use of one of the methods of Balbach, Moebius, and Thum. In the electrolytic methods the electrolyte is a silver-nitrate solution[9].

Gold Refining.—The Wohlwill process[10] of gold refining, with recovery of platinum and palladium, employs a gold-chloride solution with hydrochloric acid at a temperature of 65 to 70 degrees C. A slight modification of the Wohlwill process (55 deg. C., purer anodes, and lower current density) is in use in the United States Mints.

The applicability of the Wohlwill process to alloys richer in silver has been rendered possible by the employment of a pulsating current (obtained by superposing an alternating current on a direct current) instead of a pure direct current[11].

At the United States Mints the bullion to be parted and refined is divided into two classes by selection and blending. The first class is largely gold and is treated as stated above. The second class contains largely silver, the anodes being composed of 300 parts of gold per 1000 total, and 700 parts of silver, copper, etc.; the electrolyte is a 3 percent solution of silver nitrate with 1.5 percent free nitric acid. A very small amount of gelatine is added to obtain the silver deposit in coherent form[12].

Lead Refining.—The Betts process[13] employs a solution of lead-fluosilicate, containing an excess of fluosilicic acid (5 to 7 percent Pb and 12 to 15 percent Si F_6) with a very small addition of gelatine or glue, depositing lead in dense coherent form and free from bismuth. The voltage per tank is 0.35 to 0.4, including losses; the temperature 30 degrees C.; the energy consumption from 5½ to 6 horsepower-days per ton of lead.

Nickel Refining.—Either a chloride or sulphate electrolyte may be employed. F. Foerster recommends a temperature of 60 to 70 deg. C., good circulation and a current density of 0.01 to 0.02 ampere per sq. cm., with a solution containing about 30 grams nickel (= 145 grams $NiSO_4$, 7 H_2O or 121 grams $NiCl_2$ $6H_2O$) or more per liter. The nickel deposit is of such density and tenacity that it may be rolled immediately into form of sheets. D. H. Browne[14] obtained good coherent deposits from a neutral solution containing 70 grams $NiCl_2$, 180 NaCl per liter, heated to 50 to 75 deg. C., with a current density of 100 to 200 amp. per

sq. m. with efficient circulation of electrolyte. From sulphate solutions, thick cathodes may be deposited, with a solution of neutral nickel sulphate or nickel-ammonium sulphate, kept at about 50 deg. C. with efficient circulation and a current density of 50 to 300 amp. per sq. m.

Zinc Refining.[15]—In the Hoepfner process, which is in use in a plant in England, a zinc chloride solution is subjected to electrolysis[16]. The latest advance[17] of the Siemens & Halske Co. in this field is the use of manganese-peroxide anodes. The power consumption is 3.4 kw-hr. per kilogram of zinc.

Iron Refining.—The Burgess process[18] of producing 97 to 99 percent pure iron, free from carbon (the chief impurity being hydrogen), employs a solution of ferrous and ammonium sulphates with a cathodic current density of 6 to 10 amperes per sq. ft. and a slightly smaller anodic current density. The e.m.f. for each cell is slightly below 1 volt; the temperature of the electrolyte is 30 deg. C.; the anodes consist of ordinary grades of wrought iron and steel. Iron, refined by the Burgess process, has served as the starting material in extended researches on the properties of iron alloys free from carbon. Pure iron of this kind is very hard.

Tin Refining.—Claus[19] electrolyzes raw tin (containing at least 90 percent tin) in a 10 percent sodium sulphide solution at a temperature of more than 80 deg. C., with a current density of 0.5 amp. per sq. cm. at a voltage at the electrodes below 0.2 volt. The electrolyte is not circulated. Before introducing new tin anodes into the cell, it is necessary to dissolve in the electrolyte about 1 percent of its weight of sulphur, preferably in form of flowers of sulphur.

Bismuth Refining.[20]—Anodes containing over 90 percent Bi, besides lead, silver, etc., are refined in a cell similar to that used in the Balbach silver refining process, with an electrolyte containing free hydrochloric acid (7 percent Bi and 9 to 10 percent HCl). The cathodic current density is 20 amp. per sq. ft., the anodic current density is three times this amount; the voltage at the electrodes is 1.2. Silver and gold remain at the anode, but traces of silver pass into the bismuth deposit. The product is 99.8 percent pure, the chief impurity being silver.

Cadmium Refining.[21]—A cadmium sulphate solution containing free acid is electrolyzed with a current density of 0.005 to 0.05 amp. per sq. cm.

2. Electrolysis with Insoluble Anodes. While in processes with soluble anodes the metal to be won or purified is at the start in the anode, it is in the electrolyte in processes using insoluble anodes; therefore, in most cases the electrolytic process is preceded by a leaching process which brings the metal into solution.

Gold.—The classical example of such a process is the Siemens & Halske process of electrolytic precipitation of gold from cyanide solutions which was in successful commercial use for years in South Africa, but was replaced in the end by zinc precipitation. For a full account[22] see the paper by Clevenger before the American Electrochemical Society, San Francisco meeting, September, 1915.

Copper.—The first attempts of using electrolysis with insoluble anodes on a large scale were, however, made with copper ores, in the processes of Siemens & Halske and of Hoepfner, a sulphate solution being used in the former, a chloride solution (doubling the weight of the deposit per ampere-hour) in the latter. These experiments were extended to other metals, especially nickel and zinc, but all these early experiments failed, and the result was that the hydrometallurgy of copper was regarded somewhat with suspicion, until during the last few years the tables have been turned and new experiments on the leaching of low-grade copper ores and tailings have set in, which in several cases have led to the erection of commercial plants. These various processes differ in the method employed for precipitation, since, besides electrolytic precipitation, hydrogen sulphide and pig iron have been used as precipitating agents. In recent time electrolytic precipitation has found more and more favor. This brief note must suffice here, since copper leaching is the subject of a separate paper by W. L. Austin before this Congress[23].

III. ELECTROLYTIC-FURNACE PROCESSES.

In electrolytic furnace processes both the heating effect and the electrolytic decomposition effect of the electric current are utilized. For heating, either direct current or alternating current

may be utilized; for electrolytic decomposition, direct current must be used. Hence in electrolytic-furnace processes either direct current or pulsating current (a superposition of direct and alternating current) must be employed.

As the fundamental principles of the heating effect of the electric current and of electrolytic decomposition have been fully discussed in the preceding chapters, and are valid without modification for electrolytic furnaces, it will be sufficient to review the different metals produced by electrolytic furnace processes.

Aluminium.[24]—In the processes of Hall and Heroult the electrolyte is a fused solution of alumina (as solute) in the double fluoride of aluminium and sodium (as solvent). Carbon anodes are used, while the melted aluminium metal in the bottom of the pot forms the cathode. The temperature is 900 deg. C. The alumina is decomposed by the current and fresh alumina is added at intervals to the bath. According to J. W. Richards, the production of 1 kg. of aluminium requires 22 kw-hr. As to the industrial uses of aluminium, see the paper by J. W. Richards, before this Congress.

It is hardly to be expected that great improvements will be made in the electrolytic process itself, but cheaper methods may be found for providing the starting material, pure alumina. A promising possibility is the Serpek process[25] which is being tried on a large experimental scale in France. Its principle is, first, the production of aluminium nitride, AlN, from impure alumina and carbon in an electrically heated kiln in an atmosphere of nitrogen or producer gas at a temperature between 1600 and 2000 deg. C. This is followed by the decomposition of the aluminium nitride by water or caustic soda solution, thereby liberating the nitrogen as ammonia and producing an alkaline aluminate solution from which pure alumina can be obtained.

Sodium.—The classical process for making metallic sodium on a large scale is that of Castner, in which a fused Na O H electrolyte is used at a temperature not more than 10 or 15 deg. C. above the melting point (which is at 308 deg. C.). A gauge or screen is provided between the electrode and a superposed dome for collecting the metallic sodium. The principal object in the

development of new sodium processes has been to use the cheaper sodium chloride instead of sodium hydroxide, as starting material[26].

Magnesium.—Magnesium[27] is produced by electrolysis from a fused dehydrated bath of carnalite, i. e., a double chloride of potassium and magnesium, or from a fused bath of magnesium chloride.

Calcium.—Metallic calcium[28] is made by a process of the Allgem. Elek. Ges. by electrolysis of fused calcium chloride, the cathode being continually and slowly raised during electrolysis, so that its end always just touches the surface of the bath.

Cerium.—Cerium[29] is made electrolytically from the residue of the Welsbach gas mantle factories, by a process of Auer von Welsbach. Cerium-iron is a pyrophoric alloy.

Zinc.—A great many attempts have been made to treat complex sulphide ores which contain zinc, with chlorine, producing zinc chloride, separating it from the other chlorides and electrolyzing, but commercial success has not yet been attained[30].

APPENDIX.

[1] A useful summary of the status of "the electric furnace in metallurgical work" is given by D. A. Lyon, R. M. Keeney, and J. F. Cullen in Bulletin 77 of the Bureau of Mines, with very full references to original articles published in periodical literature. A good general book on electric furnace construction and applications is Stansfield's "The Electric Furnace". Also different chapters of Askenasy's "Einführung in die technische Electrochemie" and in Allmand's "Principles of Applied Electrochemistry" (a very good all-around book) should be consulted.

[2] Rodenhauser and Schoenawa, "Elektrische Oefen in der Eisenindustrie"; Lyon and Keeney, "Electric Furnaces for Making Iron and Steel", Bulletin 67, U. S. Bureau of Mines; Helfenstein's chapter in Askenasy, "Einführung in die Technische Elektrochemie". The most important publication on the early work in the electrometallurgy of iron and steel is Haanel's first Canadian Government report (1904). A very good review of the situations in 1909 may be found in the symposium of papers on the electrometallurgy of iron and steel in Transactions American Electrochemical Society, vol. XV.

[3] The most important early literature on the subject comprises E. Haanel's second and third Canadian Government reports; also papers by Haanel, Bennie, Lyon, Richards in Trans. Am. Electrochem. Soc., vol. XV. Concerning later developments in Scandinavia and California, see the numerous articles in Metallurgical and Chemical Engineering.

[4] Pointed out by J. W. Richards (Metallurgical and Chemical Engineering, vol. X, pp. 397 and 539).

[5] Besides the extensive literature in technical periodicals (especially Engineering and Mining Journal, Electrochemical and Metallurgical Industry, Metallurgical and Chemical Engineering) see chapter 12 in Stansfield's "Electric Furnace".

[6] A standard work on the theory and practice of the electrolysis of aqueous solutions is Foerster's "Elektrochemie wässeriger Lösungen" (second edition, only available in German). The relative chapters in Allmand's "Applied Electrochemistry" and in other general books on electrochemistry like those of Hopkins, McMillan and Cooper, Perkin, and M. deKay Thompson should also be consulted.

[7] A very useful and comprehensive set of papers, summarizing all the different solutions proposed and used for plating with gold, silver, cobalt, nickel, lead, tin, copper, brass, and bronze may be found in vol. XXIII of the Transactions of the American Electrochemical Society.

[8] As engineering applications of the principle of electrotyping should, however, be mentioned the Elmore process of producing seamless copper tubes and the Cowper-Coles process for producing pure iron sheets and

tubes (see Palmaer and Brinell, Metall. and Chem. Eng'ing., Vol. XI, p. 197). Besides bringing the metal by electrolytic deposition into the desired form, both processes also involve the principle of electrolytic refining.

[9] For a description and critical comparison of the different methods see Easterbrooks, Transact. Amer. Electrochem. Soc., vol. VIII, p. 125; Electrochem. and Met. Ind., vol. VI, p. 277; Kern, Met. and Chem. Eng., vol. IX, p. 443.

[10] Wohlwill, Electrochem. Ind., vol. II, pp. 221 and 261, vol. VI, p. 450; Tuttle, Electrochem. Ind., vol. I, p. 157; vol. VI, pp. 355 and 408; Kern, Met. and Chem. Eng'ing, vol. IX, p. 446.

[11] Met. and Chem. Eng'ing, vol. VIII, p. 82.

[12] Tuttle, Electrochem. and Met. Ind., vol. IV, p. 306.

[13] See Betts' book on "Lead Refining by Electrolysis".

[14] Electrochem. Ind., vol. I, p. 348.

[15] See Günther's German monograph, "Darstellung des Zinks auf elektrolytischem Wege".

[16] Concerning the few details of operation which are known, see W. Koehler, Electrochem. Ind., vol. I, pp. 540, 568, and Allmand's "Applied Electrochemistry", p. 286.

[17] Engelhardt, Met. and Chem. Eng'ing, vol. XI, p. 43.

[18] Burgess, Electrochem. Ind., vol. II, p. 183; Kern, Trans. Am. Electrochem. Soc., vol. XIII; also Foerster, Mustad and Lee, Abhandlungen Bunsen Gesellsch., vol. 2, p. 34; Pfaff, Zeit. f. Elektrochemie, vol. 16, p. 217.

[19] Steiner, Electrochem. and Met. Ind., vol. V, p. 309.

[20] Mohn, Electrochem. and Met. Ind., vol. V, p. 314.

[21] Mylius and Funk, Zeit. f. anorgan. Chem., vol. 13, p. 157.

[22] Concerning the unsuccessful attempt of Clancy to develop a cyanamide process, combined with electrolysis, as a substitute for the cyanide process, see Met. and Chem. Eng'ing, vol. VIII, pp. 608, 623; vol. IX, pp. 21, 336. Electrolytic amalgamation has been experimented with repeatedly, but is not in use on a large scale at present; the principle is to make the mercury in the ordinary amalgamation process cathode in an electrolytic cell. See Carey, Met. and Chem. Eng'ing, vol. VIII, p. 438, Trans. Am. Electrochem. Soc., vol. XIX, p. 127.

[23] Concerning the early work of Hoepfner, see Koehler, Electrochem. Ind., vol. I, pp. 540, 568. Concerning the Siemens and Halske process, see Electrochem. Ind., vol. II, p. 225. Concerning the process of D. H. Browne, for the separation of copper and nickel, which was in successful commercial use for a number of years in Cleveland, Ohio, see Haber, Electrochem. Ind.,

vol. I, p. 381. Concerning electrolytic processes in zinc metallurgy see W. McA. Johnson, Electrochem. and Met. Ind., vol. V, p. 83; also Transact. Amer. Electrochem. Soc., vol. II, and J. W. Richards, Transact. Amer. Electrochem. Soc., vol. XXV; also Günther's Darstellung des Zinks auf Elektrolytischem Wege.

[34] J. W. Richards' "Aluminium" is the standard book on this metal; concerning the theory of the process, a different view is defended in the book by Minet, translated by L. Waldo.

[35] Tucker and Read, Trans. Am. Electrochem. Soc., vol. XXII, p. 57; Richards, Met. and Chem. Eng'ing, vol. XI, pp. 137 and 281; Tucker, Met. and Chem. Eng'ing, vol. XI, p. 139; Fraenkel, Zeit. f. Elektrochem, vol. XIX, p. 362.

[36] A good summary of various sodium processes is given by C. F. Carrier, Jr., in Electrochem. and Met. Ind., vol. IV, pp. 442, 475; also Met. and Chem. Eng'ing, vol. VIII, p. 253. Concerning the process of Seward and Kügelgen see Electrochem. and Met. Ind., vol. V, pp. 56, 238, 470; concerning the process of Ashcroft, see Electrochem. and Met. Ind., vol. IV, p. 218.

[37] Tucker and Jouard, Trans. Amer. Electrochem. Soc., vol. XVII, p. 249. Frary and Berman, Met. and Chem. Eng'ing, vol. XIII, p. 324. Concerning the process of Seward and Kügelgen, see Electrochem. and Met. Ind., vol. V, p. 470; vol. VI, pp. 160, 465; vol. VII, p. 495.

[38] J. H. Goodwin, Electrochem. and Met. Ind., vol. III, p. 80; Frary, Trans. Am. Electrochem. Soc., vol. XVIII, p. 117; Seward and Kügelgen, Electrochem. and Met. Ind., vol. VI, p. 160.

[39] Hirsch, Transact. Am. Electrochem. Soc., vol. XX, p. 57.

[40] Concerning the Swinburne-Ashcroft process, see Electrochem. Ind., vol. I, p. 412; vol. II, p. 404; vol. IV, pp. 91, 143, 178, 357. Concerning the Baker-Burwell process, Electrochem. and Met. Ind., vol. V, p. 448; Met. and Chem. Eng'ing, vol. VIII, p. 690. Concerning the Malm process, Met. and Chem. Eng'ing, vol. XII, p. 128. A standard work on electrolysis of fused salts in general is Lorenz' "Elektrolyse geschmolzener salze", 3 vols.

Paper No. 194

METALLOGRAPHY.

By

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The field of Metallography during the last fifteen years has broadened from a study of the structure of metals and alloys, together with the thermal diagram, so that it now embraces the structure and constitution of metals and alloys and their relation to the physical and chemical properties.

We now possess several excellent texts, such as Desch's "Metallography", Gulliver's "Metallic Alloys", Guertler's "Metallographie", and Rosenhain's "Introduction to Physical Metallurgy". The "Internationale Zeitschrift für Metallographie", edited by Guertler (Borntraeger, Leipzig) is now in its seventh volume, while the "Journal of the Institute of Metals" (London), in its twelfth volume in 1914, devotes much of its space to the science. The abstracts of these two journals cover the whole field of non-ferrous work, the former embracing also the ferrous side, which is also dealt with in the abstracts of the "Journal of the Iron and Steel Institute" (London). The list of books and periodicals given later is not intended to be exhaustive, but gives the chief publications of interest.

To give a complete review of the work in Metallography for even the last few years would be a task of considerable difficulty, first because of the enormous mass of material, and secondly, because of the impossibility of presenting it logically. It was therefore decided to treat the subject as follows:

Metals—Structure and Physical Properties
Binary Alloys—Constitution, Properties
Ternary Alloys—Constitution, Properties
Miscellaneous: Alloys—Uses

Electrical Properties

Corrosion

Sulphides, etc.—New Applications of Metallographic Methods

Recent Books.

Heyn's "Report on the Progress of Metallography during 1909, 1910, and 1911", gives 540 titles and may be used as a starting point.*

METALS.

The Structure of Metals.

The old ideas of the structure of metals were based on fracture, and from this came the terms—crystalline, granular, fibrous, and amorphous. In general, all metals are crystalline and the fracture may have no relation to the structure, and depends not only on the method of breaking but also on the mechanical and thermal treatment. All metals solidify as crystalline grains with distinct orientation, the size and shape depending chiefly on the rate of solidification and the thermal gradient within the freezing mass.

When strained within the elastic limit, the structure shows no change, but when this is passed there is a permanent deformation, and within the grains themselves we find slip-lines and slip-bands, which increase in number and direction as the strain increases, and the grains are distorted and elongated. The elastic limit is greatly increased and the metal becomes harder, but the ductility falls off as a rule.

On reheating such strained metal, a temperature is reached where the elastic limit and hardness show a rapid falling off and the ductility returns. The grains rearrange themselves and begin to grow with distinct polygonal boundaries, with frequent twinning, the size depending on the temperature and time of annealing, the amount of cold-work the metal has undergone, and upon its cross-section. Copper is annealed at 200° C. (Grard), gold softens above 100° C. (Rose), silver begins to soften after 4 hours at 100 ° C. (Hanriot and Lahure), while lead and zinc may soften at ordinary temperatures.

The structure of hot-worked metals consists of polygonal

* International Association for Testing Materials, Vol.1, 1912. II-I.

grains, more or less twinned, and closely resembles that of annealed metal. This is due to the fact that there is enough heat present, after distortion of the grains, to cause annealing. In general, the greater the reduction and the lower the temperature, the finer the grains. A point is reached where the temperature is too low to cause annealing, the grains remain distorted and cold-work may be said to have begun. This critical temperature varies widely—for tungsten it is over 1300° C., for zinc below 150° C.

The Amorphous Theory. Beilby has shown that in the process of polishing, a thin film of metal actually flows like a liquid, and is apparently an amorphous modification. He has put forward the theory that cold-working of metals produces an amorphous film on the surfaces of slip-planes, which modification is harder and stronger than the original crystalline one. Reheating to the annealing temperature causes the transformation from the amorphous to the crystalline state, and the hardness falls and ductility returns in consequence. Studying the mechanism of intercrystalline cohesion, Rosenhain and Ewen have brought forward the "amorphous cement" theory, which states that the crystals of metals are cemented together by an extremely thin layer of non-crystalline material which has distinct physical properties. The amorphous theory is opposed by Tammann, Heyn and others.

Strain Disease. Cohen shows that in cold-worked metals we are dealing with metastable systems. The size of grain can be increased by inoculation from normal metal by means of an etching agent.

Quincke's "Foam-Cell" Hypothesis. The process of crystallization begins with the separation of the liquid into two immiscible liquid phases. The one which is present in relatively small amounts so arranges itself as to form the walls of "foam-cells", which may be very thin and invisible, filled with the liquid present in greater quantity, after the manner frequently seen in immiscible oils and aqueous solutions. These "foam-cells", according to their form and size, determine the arrangement of the crystalline particles when actual solidification takes place. Hard-drawn wire contains many invisible cylindrical foam walls, and therefore possesses great strength. Annealed

wire has less strength because, on heating, the viscosity diminishes and foam walls contract to form drops.

Melting-points. Critical Points. The melting-points of the metals have now been determined with great accuracy and are given by Burgess. According to Pirani and Meyer, W melts at 3100 ± 60°; Mo, 2450 ± 30°; Ta, 2850° C. According to Ruff we have: Au = 1071°, Mn = 1247°, V = 1715°, Cr = 1514°, Pt = 1750°, Mo = 2110°, Ir = 2224°, W = 2575°. Ruer gives Ni = 1451, Co = 1491.

The "critical points" of iron are 900 and 780° C. Nickel transforms at 360° C. Cobalt at 1102° C. According to Cohen, copper transforms at 71.7° C.; zinc, 300-350 and possibly at 170° C.; cadmium at 64.9° C.; tin at 18 and 161° C.

Tiede and Birnbraüer, working in vacuo, found the volatility of Sn at 880, Ag at 830, Cu at 1360, Ta at 2200, W at 2450° C.

Physical Properties.

A great deal of research has been done, especially in regard to determining the effect of cold-work and of annealing on strength, ductility and hardness. Many of the references given include work on alloys also.

The strength and hardness of Al up to 300° C. is given by Baumann, while the tensile properties of Cu at high temperatures are given by Bengough and Hudson, by Huntington and by Hughes.

Tungsten. The use of tungsten in lamps and for electrical heating purposes is now well established. The preparation of the metal in the ductile condition is of comparatively recent date. The behaviour of the metal is peculiar, and during the hot-working, changes from a state of extreme brittleness to one of comparative ductility, which as yet has not been explained from its structure. Annealing between the stages of hot-work seems to have very little tendency to cause a rearrangement of grain, which remains drawn out and elongated. On the other hand, the filament of a lamp after use is found to be entirely recrystallized and consists of a string of coarse crystals, which causes more or less brittleness compared with the original wire. The preparation of the wire in ductile form from a rod of pressed tungsten powder, consists in first sinter-

ing the rod at a very high temperature by the passage of an electric current in an atmosphere of hydrogen, then swaging it very hot until it can be drawn hot through diamond dies into the finest wires. The reheating between the various passes in swaging is done in hydrogen.

BINARY ALLOYS.

The thermal diagrams of most of the binary alloys have been worked out and are given in Guertler's "Metallographie", and by Bornemann, Desch, Gulliver, etc. The theoretical discussion of the various type diagrams is already well understood and given in the main text-books. The determination of the diagrams themselves has been in many cases faulty, and new work is constantly being done upon them, considerably modifying our original ideas. This is especially true of the changes which take place in the solid state, theoretically discussed by Heyn and others. For example, the alloys of lead and tin, of aluminum and zinc, were long given as examples of the simplest class of binary alloys. Recent researches have shown that the former undergo profound changes in the solid, while the latter, in addition, form a compound by reaction during the process of freezing, which has hitherto escaped detection.

Thermal Diagrams.

From the references below, one or two papers deserve mention. Carpenter has shown the similarity between the three series, Ag-Zn, Cu-Zn and Ag-Cd. Mazzotto's work on Cd-Sn shows a eutectoid at 130° C. and 94.5% Sn. Cobalt alloys have been studied by Waerlert, Ruer and others, while Ruer's work on Cu-Fe shows a new horizontal on the iron branch at 1440° C., similar to that in the Fe-Co alloys.

Konstantinoff and Smirnoff in the Sb-Sn alloys show two compounds, Sb-Sn and Sb_3Sn_2. The alloys of silver and gold with tellurium have been studied by Pellini and Quercigh, who found Ag_2Te: Ag Te: and Au Te_2.

The alloys of carbon with Co, Ni and Mn have been examined. Cobalt dissolves 3.9% C. at 1700° C., which separates as graphite. There is a eutectic at 2.8% C. and 1300° C., at which temperature 0.82% carbon is in solid solution, falling to

0.3% at 1000° C. A carbide has not been detected. Nickel dissolves 6.42%C. at 2100° C. (Ni_3C). The carbide is unstable and breaks up into Ni + Graphite. There is a eutectic at 1310° C. and 2 to 2.5%C. when Ni holds about 1%C. in solid solution.

Joyner has studied the structures of the silver-tin amalgams.

The Cu-Cu_2O diagram has been completed by Slade and Farrow. It resembles Cu-Cu_2S. Mathewson and Stokesbury find that the Ag-Cu_2O series is very similar to that of Cu-Cu_2O. It shows a eutectic of 1.3% Cu_2O at 945° C.

Copper-Zinc. The brasses, due to their commercial importance, have had a great deal of attention. The original diagram of Shepherd was modified by Carpenter and Edwards, whereby the beta constituent which occurs from 36 to 60% Zn, undergoes a transformation at 450° C., tending to break down into alpha and gamma, a eutectoid change. The recent work of Hudson seems to indicate that the diagram is even more complex than that given by Carpenter and Edwards. The physical properties, effect of hot and cold work, and of annealing and their relation to the microstructure have been carefully studied by Lohr, Webster, Grard and others, with the result that we are beginning to see that the relation between structure and properties is very close.

The effect of other metals on typical brasses has been studied, especially in the case of certain so-called "bronzes"—e. g., manganese bronze, tobin bronze, etc.—with the result that the new alloys have a much greater strength, yet retain their ductility.

Copper-Tin. The bronze diagram first worked out by Heycock and Neville, then modified and completed by Shepherd and Blough, has again been under discussion, notably by Hoyt and by Haughton. Much remains to be done before the actual diagram is settled. That part of the diagram embracing the useful alloys is complete, however. As in the case of the brasses a great deal of study has been devoted to their physical properties, effect of work, and of annealing. The effect of the presence of Cu_4Sn or delta is now well understood. The effect of small amounts of other metals has also been studied, notably

for the alloy 88 Cu 10 Sn 2 Zn or Admiralty bronze, and various phosphor bronzes.

Copper Aluminum. These alloys have also had considerable attention, first the copper-rich or "aluminum bronzes", second the light aluminum alloys. The copper end of the diagram is still under discussion. Their properties have been carefully worked out by Carpenter and Edwards in the 8th report to the Alloys Research Committee. The light alloys for automobile and other work have developed considerably and we have such alloys as "Duralumin".

Aluminum Alloys. The Zn-Al alloys, due to their properties, have long been used. Their diagram and properties have been thoroughly worked out by Rosenhain and Archbutt in the 10th report to the Alloys Research Committee. They discovered a definite compound, Al_2Zn_3, which forms by reaction with the melt at 445° C. It decomposes however at 256° C. into zinc and the Al-Zn solid solution, which explains some of the peculiarities of Al-Zn castings. The pressure of manganese seems helpful, while small amounts of magnesium confer the property of hardening, which appears some time after quenching.

HEAT-TREATMENT. ANNEALING. PROPERTIES AT HIGH TEMPERATURES, ETC.

A general review of the subject of heat-temperature is given by Portevin, who points out that it depends on the tendency to return to a state of mechanical, chemical or crystalline equilibrium. Cold-worked alloys rearrange their distorted constituents on annealing, while those whose rate of freezing or of cooling was such that they were in a state of metastable equilibrium tend to become stable. Inhomogeneous grains of a solid solution become homogeneous, often dissolving a second constituent up to their saturation point, as in the case of gun-metal, where delta disappears on annealing.

The annealing of brass and bronze has already been referred to. Rose has investigated the heat treatment of the alloys used in coinage; Webster worked on monel metal, aluminum-bronze, cupro-nickel, brass, etc.

The change in strength and ductibility of alloys when heated has been investigated by several. Huntington found that while the tensile strength falls off directly with the temperature, for bronze the elongation and reduction of area take a dip at 400° F., with a minimum between 600° and 700° F. For brass, the elastic limit shows a maximum at 400° F., the elongation a maximum at 500° F., at which point the reduction of area begins to dip. For copper-nickel, the elongation begins to dip at 400° F. and the reduction of area shows a maximum at 350° F. For copper-aluminum the elastic limit rises slightly to 800° F. and then falls: the elongation takes a sharp dip at 400° F. to a minimum at 800° F. The reduction of area slowly falls to 400°, then sharply, with a minimum at 800° F.

The process of cementation or diffusion in the solid has had considerable study in iron and steel. Bruni has studied the diffusion of copper into nickel, and into gold, also silver into gold to form solid solutions. Conditions were studied by measuring the change in electrical conductivity. Diffusion of copper and zinc is considered by Hudson.

The behaviour of alloys when heated in vacuo has been dealt with by Turner and others, more especially the brasses. When zinc is present in amounts of less than 40%, it can be distilled off, leaving all the copper behind.

The autogeneous welding of alloys has been studied by Carnevalli. In copper the capacity to resist fracture is reduced 50%, brittleness increases 30%, and ductibility falls to one-tenth of the original. In brass and bronze the deficiency in mechanical properties is greatly intensified as the number and variety of constituents increase. While mechanical treatment of the weld causes no improvement, heat treatment is beneficial, especially slow-cooling. Loss of tin and zinc is large, and oxides dissolve in the metal. For aluminum a coarse crystallization results, inducing brittleness. Hammering and reheating to 500° C. gives great improvement.

TERNARY ALLOYS.

The ternary systems are now being extensively investigated. The ternary diagrams have been theoretically discussed by Heyn, Geer, Janecke, etc. Many investigators express composition in

atomic percentage, while the majority use percent by weight. Graphic methods of conversion from one system into the other have been published by Hoffmann, giving a great saving of time.

A great deal has been accomplished during the last few years in unravelling the constitution of ternary alloys. Tafel worked out the Cu-Nu-Zn diagram, applied to the German silvers; Hudson and Law the phosphor-bronzes; Hoyt the copper-rich Kalchoids; Giolitti and Marantonio the plastic bronzes; Edwards and Andrews the Cu-Sn-Al diagram and properties.

Other systems have been investigated in part, as the copper end of the Cu-Zn-Al diagram by Carpenter and Edwards, of the Cu-Al-Ni by Read and Graves, of the Cu-Al-Mn by Rosenhain and Lantsbury.

The Pb-Sb-Sn system has been worked out by Loebe and by Campbell, who also investigated the tin end of the Sn-Sb-Cu series. In this connection, the work of Heyn and Bauer at Grosse Lichtefelde West is to be emphasized.

Industrially, the Ag-Zn-Pb system is of importance as bearing on the Parkes' process of desilverizing. It has been worked out by Kremann and Hoffmeier, who find the removal of zinc due to formation of Ag_2Zn_5 and not to the freezing of the zinc itself.

The importance of the formation of solid solutions in engineering alloys has been often emphasized. A number of ternary alloys are made up entirely or in part of solid solutions. Parravano and his associates have investigated the ternaries of Fe, Mn, Ni, and Cu: also the quaternary series. The German silvers are also an example. Vogel has worked on the Fe-Ni-Cu alloys and Waehlert on the system Co-Ni-Cu.

ELECTRICAL PROPERTIES.

The relation of the various physical properties to the thermal diagram has been emphasized frequently. Electric conductivity, hardness, specific weight, etc., have all been studied more or less, and the general form of their curves is known. The study of the constitution of a binary series from its electrical conductivity has been emphasized by Guertler, while different specific binary series have been investigated by Ledoux (Cu-Sn),

Pushin (Cu-Sn and Cu-As), Norsa (Cu-Zn), and Broniewski (Al alloys).

A new field of investigation has been opened up by Bornemann and his co-workers. The electric conductivity of alloys in the liquid state has been worked out for many binaries. Now this method is being used to plot equilibrium diagrams for those alloys which are only partially miscible in the liquid state. The critical temperature can be accurately determined.

MAGNETIC PROPERTIES.

The magnetic properties of Ni, Co and Fe alloys have been investigated by several, notably by Guertler, Waehlert and others already referred to under the binary alloys.

In 1903, Heussler prepared alloys of copper, manganese and aluminum and found them to be magnetic. The magnetism was explained by a ternary compound $Al_x(MnCu_8)_{\sqrt{3x}}$. Ross put forward the theory that the alloys consist of solid solutions of the binary compounds Cu_3Al and Mn_3Al, but Rosenhain showed that alloys of aluminum and manganese alone are strongly magnetic.

CORROSION.

The corrosion of brass has been the subject of a great deal of research. Two causes have been assigned: First, when the alloys are composed of the two constituents alpha and beta, there is a difference of potential between the two; the beta becomes the anode and is destroyed through the zinc going into solution, leaving a porous mass of copper behind. Secondly, when the alloy consists of homogeneous alpha, a difference of potential may be set up by adherent impurities on the surface or by strain, and corrosion begins through electrolysis. When once begun, the presence of metallic copper, which becomes the cathode to the alpha solid solution, hastens the corrosion materially and the brass is rapidly eaten through.

On the other hand, Bengough and Jones have maintained that the influence of the juxtaposition of two phases and the influence of deposits and particles are unimportant. They advocate the abandonment of the 70:30 brass for condenser tubes and the use of Admiralty mixture (70 Cu, 29 Zn, 1 Sn) or Muntz

special brass (70 Cu, 28 Zn, 2 Pb). Control of temperature and electrochemical protection are advocated. Desch and Whyte found no evidence that the presence of tin gave less tendency to corrosion. The well-known protective influence is due to the adherent deposit formed. The presence of iron accelerates corrosion. Investigating the 70:30 alloy they found, using alloys with 1% Sn, 1% Pb, and 2% Pb, the greatest corrosion with 1% Sn, the least with 2% Pb.

Bailey investigated the corrosion of aluminum. The presence of copper or sodium accelerates corrosion. Where the percentage of Si is greater than the percentage of Fe, the action is less pronounced in water or acids but more pronounced in salt solution. Water and common salt solution free from air have no corrosive action.

SULPHIDES, ETC. NEW APPLICATIONS OF METALLOGRAPHIC METHODS.

The binary alloys of the metal and its sulphide have been worked out in a great many cases, notably by Friedrich, Bornemann, and by Jaeger and Van Klooster. The binary alloys of two sulphides have also been studied extensively. The constitution of the series Cu_2S-FeS is still a bone of contention. Bornemann and Schreyer find four compounds, while Baykoff and Troutneff's curve show a series of solid solutions with a minimum at 45% Cu_2S and 956° C. These differ markedly from the older results of Rontgen and of Hofman.

The binary alloys of the metal and arsenic have also been studied in a great many cases. Just as the Cu_2S-FeS series is important in the study of Mattes, so is the Co-Ni-As series to the study of speisses. The system has been examined by Friedrich, who has determined the ternary freezing surface for Co,-Co As,-Ni As,-Ni.

The study of rock-formation, slags, Portland cement, etc., has led to a lot of preliminary work along metallographic lines. The work of the Geo-Physical Laboratory, Washington, stands out in this line. The first six references are typical of their research. Shepherd and Rankin have given us the ternary diagram for the CaO-Al_2O_3-SiO_2 series, with a study of Portland cement clinker.

Lastly, the application of metallographic methods to the study of opaque ores is yielding valuable results. Along this line, two papers, those of Graton and Murdock, and of Singewald need special attention, as indicating the results which can be obtained.

RECENT LITERATURE.

Until comparatively recently no systematic presentation of the whole field of Metallography was attempted. Information had to be sought at the original sources, such as the "Zeits. für anorganische Chemie" and the "Zeits. für physikalische Chemie", the "Revue de Metallurgie", "Metallurgie," now "Ferrum", and "Metall und Erz", and elsewhere.

Now we have Guertler's "Text-book of Metallography", Vols. I and II, Desch's "Metallography", Gulliver's "Metallic Alloys", Rosenhain's "Introduction to Physical Metallurgy", and a number of smaller works. Some of the more recent are given below. As a starting point to find the literature on any subject, the abstracts in the "International Journal of Metallography" and in the "Journal of the Institute of Metals", London, cover the field exceedingly well.

Paper No. 195

SYMPOSIUM ON THE UTILIZATION OF FUELS IN METALLURGY.

Edited by

C. H. FULTON, Mem. A. I. M. E.
Professor of Metallurgy, Case School of Applied Science
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PULVERIZED COAL IN REVERBERATORY FURNACES.

By

D. H. BROWNE, Mem. A. I. M. E.
New York, N. Y., U. S. A.

In December, 1911, the Canadian Copper Company commenced to use pulverized coal in reverberatory furnaces. As originally built, these furnaces were 112 ft. x 19 ft. hearth area. The extreme inside height, 6 ft. The bottom was an inverted arch of magnesite brick.

The coal was first cracked to ½ inch size, then dried in a Ruggles coal dryer, and finally crushed to a 200-mesh powder in Raymond impact pulverizers. This powder was blown into the furnaces through five nozzles into which it was conveyed by screw conveyors in front of a low pressure fan blast.

Operations during the years 1912-13 showed that the furnace as originally designed, along the old lines of grate fired reverberatories, was not adapted to the use of a powdered fuel which burned almost exactly like oil. The roof, exposed to such an intense flame, required frequent repairs. In the fall of 1913, the design was changed. A silica bottom, as used at Anaconda, replaced the inverted arch as a hearth. The roof was raised, making a combustion space 6 ft. 3 in. high above the skimming line. The side doors were bricked up and the charging system changed to feed almost the entire charge from

two continuous hoppers, through 6-inch pipes, 18 inches apart, which are inserted in the roof at the intersection of the side walls. The charge thus forms a continuous embankment which protects the sides and prevents the introduction of air into the smelting space, except as supplied through ports between the coal burning nozzles. This careful regulation of air supply, and the almost continuous feeding of the charge along the side walls, result in an increased ratio of charge to fuel.

During the first three months, in 1914, the monthly average of tons charge smelted, per ton coal used, was 5.0, 5.65, and 6.77. In other words, in March, 1914, 6.77 tons charge was smelted with one ton pulverized coal.

Coal ash does not settle either upon the charge or in the flues to any extent such as would interfere with the operation. The examination of the flues and the removal of a small amount of clinkered ash from the throat take only a few minutes' time every morning and do not necessitate stopping the fuel supply. Part of the waste heat is used to supply steam for heating offices and shops, but as electrical power is plentiful, no attempt has been made to use the flue gases for power.

However, this point has been carefully gone into, and the study indicates that, with the proper installation of waste heat boilers, practically 50% of the value of the fuel could be recovered in power.

BURNING PULVERIZED COAL IN COPPER REVERBERATORIES.

By

E. P. MATHEWSON, Mem. A. I. M. E.
Anaconda, Mont., U. S. A.

Quite recently it has been demonstrated that pulverized coal can be used with great success in the smelting of calcines in copper reverberatories. It has been thought that the siliceous slags of copper reverberatories, in ordinary practice, would preclude the possibility of using this excellent fuel, but a

gradual increase in silica in the content of the slag, at the Copper Cliff plant, of the Canadian Copper Company, under the direction of Mr. David H. Browne, up to 36% on some occasions, convinced Western copper smelters that a slag of even 40% silica could be made successfully in furnaces fired with pulverized coal.

The Garfield plant, of the American Smelters Securities Company, and the Washoe Reduction Works, of the Anaconda Copper Mining Company, each equipped one furnace, in the year 1914, with apparatus similar to that used at Copper Cliff, for a trial of the process. The success, in both instances, was so pronounced that both companies have ordered a change of their entire reverberatory plant over to the new system. The Garfield plant had been using fuel oil and the Anaconda plant had been using Wyoming coal, from Diamondville. The change is now being made at both plants.

This is a revolutionary step and will mean tremendous savings in operation; in fact, it is believed that, in many places, the reverberatories can be operated under the new system at considerably less cost than blast furnaces, even where the coke consumption in the blast furnace is as low as 8% of the charge.

Coals varying in ash from 5% to 23% have been used successfully in pulverized form. Two points are essential for success. The coal must be dried below 1% moisture before pulverization; and the pulverization must be carried to a very fine point. Preferably, not over 5% of the pulverized coal should rest on a 100-mesh screen, while 95% should pass through 100-mesh screen; not over 20% should rest on 200-mesh screen, while 75% should pass through 200-mesh screen.

The flame is as easy to handle as gas; the ash is caught to the extent of 50% in the flue connection between the furnace and the waste heat boiler, the balance being absorbed by the charge.

A great advantage in using the new method is that, if the charge is fed through holes in the roof, along both sides, it acts as fettling, and there is no occasion to stop the furnace and tap out for fettling. Another advantage is that the slag on the large furnaces may be discharged in a continuous stream, the same as in copper blast furnaces.

GAS PRODUCER DEVELOPMENT.

By

Z. C. KLINE
Engineer, Rhode Island Glass Co.
Central Falls, R. I., U. S. A.

During the last decade, furnace development has been largely toward regenerative and recuperative types. This is due to the large number of open hearth plants built and the general change in other furnaces from direct fire to regenerative firing. Natural gas is becoming scarcer, more expensive, and is to be had the year round only in certain localities. Oil, also, is becoming more expensive and can by no means be generally used as furnace fuel. Consequently, the gas producer has come forward by leaps and bounds, and producer gas is now being used much more generally for small furnace work as well as for the larger furnaces.

Gas producer development, recently, has been chiefly toward the mechanically operated types, and there has been a strong demand for a gas producer which would gasify bituminous coal and fix the tarry constitutents before leaving the producer.

The mechanically operated producers are much more expensive to install and probably cost considerably more for upkeep, but the labor required on them—poking the fire and breaking down clinkers—is so much less, that the labor cost is cut down markedly and a much higher class of producermen can be held. These producers also make a much more uniform gas and gasify a larger quantity of coal per square foot of surface.

Recently, there have been types of producers put on the market which claimed to fix the tarry constituents before leaving the producer. No doubt, they have accomplished this to a large extent, but they have not been perfected as yet and it is necessary to extract the tar by some auxiliary appliance before the gas is clean. Great progress has been made along this line recently and I believe that we have good reason to expect that such a producer will be developed soon, and, no doubt, this will be a great boom for power gas producers.

Within the last ten years, the development and installation of power gas producers have been of steady and normal growth. They have, however, had setbacks due to a great many installations which did not come up to expectation, and the more recent successful development of steam turbine and internal combustion oil engines. Nevertheless, gas producer plants are still being installed and are working satisfactorily. The industry has, to a large extent, lived down the bad impression given by some early faulty installations. There are a great many more competent engineers and operators in this work now than there were a few years ago, and this simplifies difficulties to a great extent.

The trend of gas producer operation will probably be toward the perfection of mechanical types and more experiments toward simplifying and cheapening the methods of obtaining clean producer gas, and, no doubt, a great deal more attention will be paid to the operation of the producers already installed, especially along lines of labor and technical efficiencies. A great many firms now have appliances for checking up quality of gas, amount of coal used, and temperature control. At last, manufacturers are realizing that a gas producer cannot be run efficiently without competent men.

SURFACE COMBUSTION (WHAT IS IT?)

By

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Air completely and homogeneously mixed with gaseous fuel, and in chemically combining proportions, constitutes a mixture that, when burned in stoves and furnaces, yields products that are free from both fuel and oxygen, and that burn at the maximum possible volumetric rate because of the absence of flame volume and regardless of the nature of the surrounding atmosphere. For commercial practicability, a definite localization of combustion zones is necessary and specific means must be provided for such control because such mixtures are

of the class termed "explosive"; i. e., have the property of self-propagation of inflammation. The fundamental physical conditions for localization are prevention of the phenomena of "back flash" and "blow off", the former being a back travel of the combustion through the mixture toward the supply, due to an inferior flow velocity as compared to that of flame propagation, while the latter, "blow off", is due to an excessive flow velocity. An additional condition to be fulfilled in commercial apparatus is the prevention of back heating from the combustion zones to the mixture supply point, along the walls of the feed passages, and, incidentally, also the suitable disposition of feed passages to yield a distribution of heat in the furnace chamber suitable for the work to be done. Back heating may be prevented by thermal resistance and by heat dissipation by cooling, the former through the use of insulating material, and the latter by abstracting heat from the walls, either internally or externally. Internal wall cooling is automatically accomplished by the flow of mixture itself, increase of specific heats of gases with temperature rise being a direct contribution, while external wall cooling may be accomplished by atmospheric air circulation about the passages, single or in groups, or by water jacketed passages in extreme cases. When most perfect cooling of passages takes place, i. e., to the point of heat abstraction at a greater rate than it can be generated in the passage, especially easy if the passages are narrow, then "back flash" is prevented regardless of flow velocity. In other cases, that is, with less complete cooling of passages, back flash is prevented by velocities obtainable by a drop in pressure through the supply exits varying from 0.1 inch water column for small passages and slow burning mixtures, to larger values for large passages and fast burning mixtures, always, however, within the range of fan pressures.

Excess exit velocity from the passages, which is normally necessary to prevent back flash, must be promptly reduced to prevent blow off, by spreading the mixture stream just beyond exit from the passages by baffles of solid refractory surfaces or by porous beds such as layers of granular refractory material, loose or bonded. These refractory spreaders become incandescent, permanent fire beds, converting a maximum of the

heat generated into the radiant form, and they incidentally act also as accelerators of the combustion reaction.

Accordingly the combustion zone may, it has been found, be definitely and permanently localized by utilizing the properties of the explosive mixtures themselves, and as a result there is now available for commercial application a new method or system of gas combustion, characterized by maximum possible rate of combustion, by maximum possible temperature of gases, because of minimum weight of products per lb. of fuel, and by products containing normally no free oxygen and no unburned fuel, though by adjustment of proportions the products may be made either oxidizing or reducing.

The fundamental principle on which the process rests was discovered by Professor C. E. Lucke, head of the Department of Mechanical Engineering, Columbia University, New York City, in the course of his doctorate research work, which was published in 1902. It was first described by him as a process for "continuous combustion of explosive gaseous mixtures", though, until 1911, no commercial applications were made by the purchasers of the patents. About this time, Prof. W. A. Bone, of Leeds University, England, made some improvements, notably in the use of bonded diaphragms as fire beds and renamed the process "surface combustion" because of the accelerating influence of the solid incandescent refractory surface. Immediately thereafter, Prof. Lucke again took up the problem and made extensive improvements after repurchasing his old patents. He then carried the process to commercial conclusions for use in domestic cooking and heating appliances (now being manufactured) and in industrial furnaces and appliances which have been designed and are about to be manufactured. The term "surface combustion" has been retained because it is appropriate not only from the point of view of Bone, who used it with reference to the action of the solid surfaces, but also as pointed out by Lucke because it is even more pertinent to, and descriptive of, the geometric form of the flame itself. This, for explosive mixtures, has length and breadth without thickness, as distinguished from the flame of non-explosive mixtures, burning in oxygen atmospheres, which is a three-dimension volume of flame, instead of a two-dimension surface flame.

DISCUSSION

Mr. Beckman.

Mr. J. W. Beckman,*** referring to the paper of Mr. Browne, asked where the ash from the coal goes.

Mr. Hamilton.

Mr. E. H. Hamilton,**** Mem. A. I. M. E., replied that at Copper Cliff, since the slag is basic, most of it goes into the slag.

Mr. Duschak.

Mr. L. H. Duschak*** said that at certain places a great deal of the ash goes up with the smoke.

Mr. Bretherton.

Mr. S. E. Bretherton,* Mem. A. I. M. E., stated that at Salt Lake 4 tons of pulverized coal gave the same results as 7 tons of good lump coal. He further stated that the ash was self-fluxing.

Prof. Clevenger.

Prof. G. H. Clevenger,** Mem. A. I. M. E., stated that at the present time there is no occasion for alarm regarding interference of the ash in coal dust firing.

Mr. Beckman.

Mr. Beckman asked why it was necessary that the coal be dry.

Mr. Braden.

Mr. E. B. Braden,† Mem. A. I. M. E., replied that it was largely on account of the difficulty of pulverizing damp coal.

Prof. Richards.

Prof. R. H. Richards,‡ Hon. Mem. A. I. M. E., asked why coal-dust firing had displaced oil firing in reverberatory practice.

Mr. Braden.

Mr. Braden replied that it was because coal dust was more efficient.

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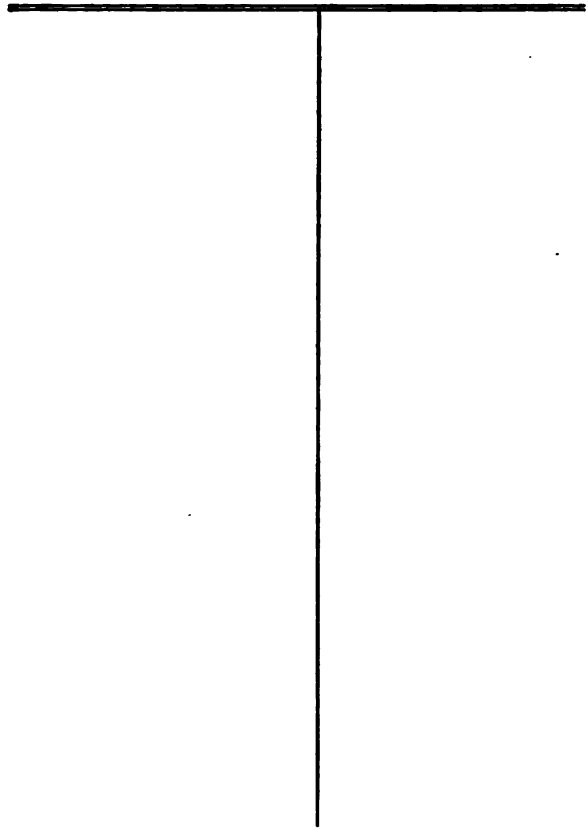

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